SYNTHETIC, PHYSICO-CHEMICAL AND ANALYTICAL STUDIES ON ANTIMONY (V) SILICATE CATION EXCHANGER

SUMMARY

Thesis Submitted for the Degree of

Doctor of Philosophy

IN

CHEMISTRY

BY

SIMA RANI

DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY,
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SUMMARY

The thesis comprises of six chapters. Chapter I is an Introduction which gives an account of the work done so far in the field of inorganic ion-exchangers with some of their salient features. It also highlights the important aspects of these materials useful for their analytical applications. At the end of the chapter an exhaustive list of important references is also given.

Chapter II summarizes the synthesis and ion-exchange behaviour of a crystalline and reproducible phase of antimony(V) silicate cation exchanger. Its stability under the chemical, thermal and irradiation treatments has also been studied. The material was synthesized under the varying conditions (Table - I) and a sample S-6 was selected on the basis of a comparative study of the ion exchange behaviour of the several samples obtained, for further study. The exchange process appears to be fast as almost all the ions are eluted out in the first 50 ml fraction of the effluent from a column of 1 g exchanger. pH titration studies indicate a monofunctional behaviour of the material, while the X-ray studies reveal its crystalline nature with the cubical crystals of a bcc system (Table-II). The presence of different functional groups and water of crystallization has been confirmed by the IR and TGA studies. On the basis of these studies a tentative

formula of antimony(V) silicate has been proposed as follows:

$$\left[Sb_2O_5 (H_2SiO_3)_6 \right].nH_2O$$

Chapter III gives an account of the kinetic studies for alkaline earths (Mg(II), Ca(II), Sr(II), Ba(II)) and transition metals (Mn(II), Fe(II), Co(II), Ni(II)) on antimony(V) silicate and antimonic acid cation exchangers. The studies have been performed at four different temperatures (25°, 33°, 50° and 65°C) under the conditions favouring a particle diffusion controlled phenomenon only. A new approach based on the Nernst-Planck equations has been applied instead of the old Bt method of Boyd. Various thermodynamic parameters such as self diffusion coefficient(Do), energy of activation (Ea) and entropy of activation (ΔS^*) have been evaluated which are useful for predicting the mechanism of the ion exchange phenomenon occurring in these materials. Table III summarizes the results of the kinetic studies.

Chapter IV summarizes the thermodynamic study of the exchanges of Mg(II), Ca(II), Sr(II) and Ba(II) with H(I) ions on antimony(V) silicate at 25° and 50°C. On the basis of the exchange isotherms, various thermodynamic parameters have been evaluated. Table IV shows the values of some thermodynamic parameters like thermodynamic equilibrium constant (K), standard free energy of exchange (ΔG°), standard enthalpy change (ΔH°) and standard

entropy change (ΔS^{o}). These studies indicate a higher affinity of the exchanger for Ca(II) and Sr(II) at 25°C and 50°C respectively. Positive values of ΔG^{o} for the Mg(II) - H(I) exchange indicate a lower preference for Mg(II) ions than for H(I) ions by the material. However for the other three exchanges the ΔG^{o} values are negative suggesting a higher preference for these ions (Ca(II), Sr(II) and Ba(II)) as compared to H(I) by the exchanger.

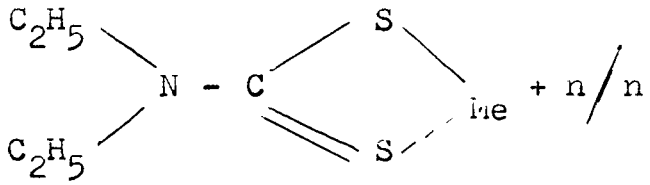
Chapter V summarizes a systematic adsorption study of alkali metal ions (Na(I), K(I), Rb(I), Cs(I)) and some other common metal ions on antimony(V) silicate in demineralized water, $HClO_4$ and DMSO + $HClO_4$ solvents. The K_d values for alkali metals vary with the pH of the solution and the material is found to be highly selective for Rb(I) at pH values $\geqslant 3$. On the basis of these studies, the utility of the exchanger has been demonstrated for some analytically important binary metal ion separations such as:

Zn(II) - Cd(II), Mn(II) - Cd(II) and Hg(II) - Pb(II).

Separation of Mg(II) from Ca(II), Sr(II) and Ba(II) has also been affected. These observations therefore, suggest that antimony(V) silicate is a useful cation exchanger.

The last chapter explores the possibility of using the antimony(V) silicate beads in spot test analysis. A sensitive and selective method has been developed for the detection of Fe(III) and Mo(VI) using sodium diethyldithiocarbamate as a complexing

reagent and the adsorptio ion-exchange properties of the material under study.[1] Diethyl dithiocarbamate forms metal complexes of the type:



Since antimony(V) sulphide is known to be an excellent collector for Mo(VI), and since antimony(V) silicate prepared in these studies has shown a high selectivity for Fe(III) and Mo(VI), the presence of Sb(V) is probably the key factor to provide an ideal base for the detection of these two metal ions. Table-V shows a comparative behaviour of some ion exchangers which includes the organic resin also. Out of the ion exchangers studied only antimony(V) silicate gives the best results in terms of the sensitivity of the test. Thorium oxide does not give any positive test probably because it is an anion exchanger while the complexes formed are positively charged. Same in the observation with an organic resin (Dowex-50 or Amberlite IR-120). A negative test with the organic resins may be attributed to their true ion exchange behaviour as against the inorganic materials which show adsorption as well as ion exchange phenomena occurring on their surfaces.

SYNTHESIS OF VARIOUS SAMPLES OF ANTIMONY(V) SILICATE CATION EXCHANGER

Sample No.	Concentration of mixing solution(M) ($SbCl_5 + Na_2SiO_3.3H_2O$)	Mixing ratio Sb : Si	Na^+ ion exchange capacity meq / g
S-1	0.5	1:1	Unstable in solution
S-2	0.4	1:1	1.6
S-3	0.3	1:1	1.7
S-4	0.2	1:1	1.5
S-5	0.1	1:1	1.7
S-6	0.1	2:1	1.6

TABLE - II

X-RAY POWDER DIFFRACTION DATA FOR CRYSTALLINE ANTIMONY(V) SILICATE

Sl. No.	2θ	Relative Intensity (in a scale of 100)	θ	Sinθ	2Sinθ	$\left(\frac{d(A^{\circ})}{n\lambda / 2\sin\theta}\right)$	$\sin^2\theta$	Indices hkl (Error)
1.	6.75	55	3.375	0.05887	0.11774	6.03620	0.00347	110 (0.0000)
2.	13.44	100	6.720	0.11702	0.23404	3.03666	0.01369	220 (0.0002)
3.	15.30	30	7.650	0.13355	0.26624	2.66940	0.01772	310 (0.0004)
4.	20.30	25	10.150	0.17623	0.35246	2.01640	0.03106	411,330 (0.0001)
5.	22.40	30	11.200	0.19423	0.38846	1.8295	0.03773	332 (0.0004)
6.	23.45	30	11.725	0.20321	0.40642	1.74868	0.04129	422 (0.0003)
7.	26.25	40	13.125	0.22700	0.45400	1.56541	0.05153	521 (0.0005)
8.	28.20	25	14.100	0.24362	0.48724	1.45862	0.05935	530 (0.0003)

The average lattice constant, a = 8.543 A°

TABLE - III

SELF DIFFUSION COEFFICIENT, ENERGY OF ACTIVATION AND ENTROPY OF ACTIVATION OF ALKALINE EARH - H(I) EXCHANGES AND TRANSITION METAL - H(I) EXCHANGES ON ANTIMONY(V) SILICATE AND ANTIMONIC ACID CATION EXCHANGERS

Sl. No.	Migrating Ion	Ionic Mobility ($m^2 volt^{-1} Sec^{-1}$)	Ionic Radii (nm)	Do, Ea and ΔS^* values					
				Antimony(V) Silicate			Antimonic Acid		
				Do ($m^2 Sec^{-1}$)	Ea (KJ $mole^{-1}$)	ΔS^* ($JK^{-1} mole^{-1}$)	Do ($m^2 Sec^{-1}$)	Ea (KJ $mole^{-1}$)	ΔS^* ($KJ^{-1} mole^{-1}$)
1.	Mg(II)	55×10^{-9}	7.8×10^{-2}	7.59×10^{-9}	15.63	-51.83	3.16×10^{-9}	12.93	-59.11
2.	Ca(II)	62×10^{-9}	10.6×10^{-2}	5.13×10^{-10}	11.13	-74.23	7.24×10^{-10}	9.72	-71.36
3.	Sr(II)	62×10^{-9}	12.7×10^{-2}	5.50×10^{-10}	11.19	-73.65	9.33×10^{-10}	10.98	-69.25
4.	Ba(II)	66×10^{-9}	14.3×10^{-2}	8.32×10^{-10}	11.24	-70.21	5.5×10^{-10}	9.17	-73.65
5.	Mn(II)	55×10^{-9}	9.1×10^{-2}	1.45×10^{-9}	12.34	-65.59	2.19×10^{-9}	12.55	-62.16
6.	Fe(II)	54×10^{-9}	8.3×10^{-2}	2.88×10^{-10}	8.94	-79.03	4.57×10^{-10}	11.15	-75.19
7.	Co(II)	55×10^{-9}	8.2×10^{-2}	8.71×10^{-9}	17.19	-50.68	3.98×10^{-9}	14.48	-57.19
8.	Ni(II)	52×10^{-9}	7.8×10^{-2}	1.58×10^{-9}	13.48	-64.87	1.95×10^{-9}	12.33	-63.12

(Average radius of the exchanger particles used = 125 μm)

TABLE - IV

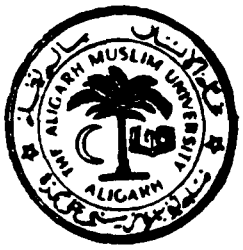
VALUES OF SOME THERMODYNAMIC PARAMETERS FOR THE Mg(II) - H(I), Ca(II) - H(I), Sr(II) - H(I) AND Ba(II) - H(I) EXCHANGES ON ANTIMONY(V) SILICATE CATION EXCHANGER

Thermodynamic parameters	Systems							
	Mg(II) - H(I) at		Ca(II) - H(I) at		Sr(II) - H(I) at		Ba(II) - H(I) at	
	25°C	50°C	25°C	50°C	25°C	50°C	25°C	50°C
K	0.07	0.12	18.33	25.96	13.68	26.95	5.35	6.64
ΔG^{o} (KJ mole^{-1})	6.70	5.63	-7.22	-8.76	-6.49	-8.89	-4.17	-5.09
ΔH^{o} (KJ mole^{-1})	19.45		11.13		21.73		6.87	
ΔS^{o} (KJ mole^{-1}deg^{-1})	0.04	0.04	0.06	0.06	0.09	0.09	0.04	0.04

TABLE - V

DETECTION LIMITS FOR IRON AND MOLYBDENUM ON DIFFERENT ION EXCHANGE MATERIALS AT ROOM TEMPERATURE (20°C)

Sl. No.	Ion exchange materials	Amount of Iron and Molybdenum detected per 0.01 ml of the test solution			
		10.0 µg	1.0 µg	0.5 µg	0.1 µg
1.	Antimony(V) silicate	+	+	+	+
2.	Antimonic(V) acid	+	+	+	-
3.	Thorium(IV) oxide	-	-	-	-
4.	Thorium (IV) phospho-silicate	+	-	-	-
5.	Tin(IV) phosphate	+	-	-	-
6.	Tin(IV) phosphosilicate	+	+	-	-
7.	Tin(IV) arsenate	+	-	-	-
8.	Tin(IV) arsenosilicate	+	+	-	-
9.	Zirconium(IV) phospho-silicate	+	-	-	-
10.	Zirconium(IV) arseno-silicate	+	-	-	-
11.	Zirconium(IV) arseno-phosphate	+	-	-	-
12.	Dowex - 50	-	-	-	-
13.	Amberlite IR-120	-	-	-	-



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K. GOPAL VARSHNEY Ph. D
ANALYTICAL LABORATORY

CHEMISTRY SECTION
FACULTY OF ENGG. & TECHNOLOGY
ALIGARH MUSLIM UNIVERSITY
ALIGARH 202001
(INDIA)

21st October, 1983.

"TO WHOM IT MAY CONCERN"

This is to certify that the work embodied in this thesis is the original work of the candidate and is suitable for the submission for the award of Ph.D. degree in Chemistry of the Aligarh Muslim University, Aligarh.

(Dr. K. C. Varshney)
SUPERVISOR

DEDICATED

TO

MY DEAR PARENTS

C O N T E N T S

A C K N O W L E D G E M E N T

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Sima Rani

(Sima Rani)

LIST OF PUBLICATIONS

1. Cation-exchange study on a crystalline and thermally stable phase of antimony(V) silicate. Effect of irradiation on ion-exchange behaviour and separation of Cd(II) from Zn(II) and Mn(II) and of Mg(II) from Ba(II), Ca(II) and Sr(II).

   Sepn. Sci. Technol., 17 (13 & 14), 1527, (1982-83).

2. Kinetics of exchange of alkaline earth metals on antimony(V) silicate cation exchanger.

   Ind. J. Chem., 22A, 657 (1983).

3. Thermodynamics of $Ca^{2+} - H^{+}$ and $Mg^{2+} - H^{+}$ exchanges on antimony(V) silicate cation exchanger.

   Acta Chimica, (In Press).

4. Thermodynamics of $Ba^{2+} - H^{+}$ and $Sr^{2+} - H^{+}$ exchanges on antimony(V) silicate cation exchanger.

   Proc. Ind. National Science Academy, (In Press).

5. Adsorption studies of alkali metals on various inorganic ion-exchange materials using radiotracers.

   Radiochem. & Radioanal. Letters, (In Press).

6. Radiation stability of some thermally stable inorganic ion-exchangers.

   J. Radioanal. Chem., (In Press).

7. Ion exchange kinetics of transition metals on crystalline antimonic acid and antimony(V) silicate cation exchangers to evaluate their separation potential.

   (Communicated to Reactive Polymers, Ion Exchangers, Sorbents).

8. Selective spot test method for the detection of Iron(III) and molybdenum(VI) on antimony(V) silicate beads.

   (Communicated to Analitica Di Chimica).

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CHAPTER - I

INTRODUCTION

Chromatography is one of the most versatile analytical techniques effective for the separation of mixture and qualitative or quantitative analysis of the separated substances. It is a separation method in which a mixture is applied as a narrow initial zone on to a stationary porous sorbent and the components are caused to undergo differential migration by the flow of the mobile phase, a liquid or a gas. The originator of chromatography was a Russian botanist Michael Tswett (1) who in 1906 separated and isolated green and yellow chloroplast pigments by column adsorption chromatography. The key features of Tswett's technique were the application of the mixture as a narrow initial zone and the development of the chromatogram by the application of a fresh solvent. His method has, however, been modified in many ways resulting in the different types of chromatography. Out of the two major types of chromatography (liquid chromatography and gas chromatography), liquid chromatography is easier to practise in ordinary chemical laboratories. In column it can be liquid-solid chromatography or liquid-liquid chromatography. If the solid stationary phase is an adsorbent the process is called liquid adsorption chromatography. If it is an ion exchange material, either organic or inorganic, it is termed as ion exchange chromatography.

Ion exchange phenomenon is not of a recent origin. The earliest of the references, it seems, is found in Holy Bible which establishes Moses' priority, who succeeded in preparing drinking water from brackish water by an ion exchange method. Later on, Aristotle stated that sea water loses part of its salt content when percolating through certain sands (2). In 1850 Thompson (3) and Way (4) discovered base exchange in soils. The materials responsible for these phenomena were identified chiefly by Lemberg (5) and Wiegner (6) as clays, glauconites, zeolites, and humic acids. Since zeolites were unstable in acid and alkaline solutions they could only be used satisfactorily under nearly neutral conditions. A more significant development took place in 1935 when Adams and Holmes (7) discovered that some synthetic high molecular weight organic polymers containing a large number of ionic functional groups, as an integral part, could be employed as ion exchangers. Such synthetic products may show cation or anion exchange properties and hence are now known as "cation exchange resins" or "anion exchange resins". They consist of a matrix which carries either a positive or a negative charge (fixed ions) and of counter ions which compensate this charge. The matrix is a highly polymerized crosslinked hydrocarbon containing ionizable groups.

If an ion exchanger containing exchangeable A ions is brought into contact with a solution containing B ions then the exchange

process may be represented as below:

$$\bar{A} + B \rightleftharpoons \bar{B} + A$$

(Barred symbols denote exchanger phase)

It is a reversible process and an equilibrium is eventually set up in which some ofthe ions initially present in the exchanger have been replaced by B ions from the solution.

The extent to which one ion is adsorbed in preference to the other i.e. the selectivity is of fundamental importance in all applications of an ion exchanger. It determines the efficiency of a process in which the ion exchanger is used to recover ions from dilute solutions and ease with which the ions can be subsequently removed from the exchanger phase. It also determines the readiness with which two or more substances, which form ions of like charge, can be separated by ion exchange chromatography. Despite significant recent advances in chromatography which have provided much information about the mechanism of separation and zone migration, the selectivity of a chromatographic system is still incompletely understood so that conditions required to separate a given mixture can not usually be theoretically predicted. The selectivity of any ion exchanger is influenced by the nature of exchanging ions such as charge, size, polarizability and hydration. In dilute solutions, ions carrying a higher charge are more strongly retained by the exchanger than the ions of a lower charge. For example for a typical ion exchanger Dowex-50 the retentions were in the

following order:

$$Na\ (I) < Ca(II) < La(III) < Th(IV)$$

The selectivity of an ion exchanger increases with the increase in the atomic number of the ions in the same periodic group i.e.

$Li(I) < Na(I) < K(I) < Rb(I) < Cs(I)$;

$Be(II) < Mg(II) < Ca(II) < Sr(II) < Ba(II) < Ra(II)$;

$F(I) < Cl(I) < Br(I) < I(I)$.

For ions of the same valency but different periodic groups the selectivity can be approximated from their activity coefficient; the greater the activity coefficient the greater is the exchange potential. Large ions, especially the organic ions, are often adsorbed strongly but full exchange capacity may not be observed. Very large molecules for example - proteins may not be able to penetrate into the resin structure and will be adsorbed on the surface only. In general the higher its polarizability and lower its degree of hydration, the more strongly will an ion be adsorbed. For example the adsorption increases from Li(I) to Cs(I) in which the degree of hydration decreases in the same direction. And also the polarizability increases with an increase in the atomic number.

The nature of an ion exchanger also effects the selectivity in two ways - it is effected by the nature of the functional group and by the degree of crosslinking of the exchanger. Exchangers containing weakly acidic and weakly basic groups are highly selective towards hydrogen ions and hydroxyl ions. Ion exchangers

containing groups which are capable of complex formation with particular ions will adsorb these ions more strongly. If the degree of cross linking increases the exchanger becomes more selective in their behaviour towards ions of different sizes. An increase in crosslinking also decreases swelling of the matrix of the exchanger.

Apart from its well known applications in inorganic analyses, ion exchange phenomenon is also applicable to the analysis of biological substances. A man contains approximately one lakh different kinds of proteins and no one knows how many different kinds of compounds. The information about the biological systems lies in these molecules, the separation of which is essential for understanding the phenomenon of living. Luckily, biological macro molecules like proteins, nucleic acids, complex polysaccharides etc. are charged (8). Introduction of the ion exchange technique for the separation of amino acids (9) led to the phenomenal development of biology. Ion exchange resins were the first ion exchange materials used for the separation of biological molecules. Several techniques like electrophoresis, gel filtration etc. have also been extensively employed for biological systems. The combination of ion exchange with such techniques led to the development of more powerful tools for such separations. For example, electrophoresis on ion exchange cellulose papers, gel filtration through ion exchanger sephadex, sepharose etc. (10).

Although organic resins are extensively utilized in medical and biochemical fields, their utility is not good at elevated temperatures and in presence of strong radiations, as they are not stable under such conditions. For this reason an interest was revived in inorganic ion exchange materials. The use of such materials for ion exchange separations has been gaining popularity (11,12). The emphesis in researches to date has been the synthesis of various inorganic compounds and experiments to characterize their ion exchange mechanism. The main use of inorganic exchangers is in the nuclear energy industry for the separation of selected nuclides from dissolved, spent reactor fuels. An ion exchange material has however, to possess several additional qualities in order to be practically useful for the purpose. The most important of these may be summarized as follows:

1. The material must be virtually insoluble within very wide limits of pH. Furthermore, it should preferably be possible to use it either in strongly acid or in fairly strongly alkaline solutions, as such media are often encountered in reprocessing work.

2. The exchange capacity must be high enough to ensure a practical operation.

3. Sorption and elution must be so rapid that columns can be operated at reasonable flow rates. This means that the polymer network must be open enought to allow a sufficiently free diffusion

of the exchangeable ions, i.e. the degree of crosslinking must not be too high.

4. The resistance to attrition must be so good that columns can be loaded and eluted many times without severe clogging or channelling.

5. It must always be possible to prepare the ion exchanger so that minor changes in the method or materials used for preparation do not cause major changes in performance.

6. The selectivity must be so high that a convenient separation between different ions, or at least types of ions, can be effected by suitable variation of pH.

7. If a separation is to be accomplished by variation of pH, another condition is obviously that the ions to be sorbed are able to compete successfully with the hydrogen ion for the functional groups, within the available range of pH.

Most of the inorganic ion exchangers which have been found to fulfil, to an acceptable extent, the fundamental qualifications given above, possess a negatively charged polymer network and thus are able to act as cation exchangers. Important examples are heteropoly acids such as ammonium molybdophosphate, complex cyanides, various acid zirconium compounds such as zirconium phosphate, molybdate and tungstate, hydrous oxides of silicon, tin(IV) and

and zirconium(IV) and also a number of basic salts of metals in high oxidation states, particularly zirconium and titanium. These materials in acid solutions show a very high selectivity for heavy alkali metals (13,14). Other materials as uranyl hydrogen phosphate (15,16), manganese(IV) oxihydrate (17), stannic phosphate (18), aluminosilicate (Decalso) (19), and clay minerats (20) are also used for the separation of caesium by a cation exchange mechanism. Important advances in this field have been reviewed by a number of workers at the various stages like Vesely and Pekarek (21,22), Alberti and Costantino (23), H.F. Walton (10,24-26), and A. Clearfield (12,27). Table I shows some important features of the large number of inorganic materials synthisized so far as ion exchangers.

Liquid ion exchangers are also receiving increasing attention these days. During the last two decades they have found large applications in various areas in analytical chemistry, mainly because of their high extraction power, versatility and reagent stability. High molecular weight amines which are commonly known as liquid anion exchangers were studied for the extraction of zinc, cadmium and mercury. Cadmium and mercury are the serious pollutants of the biosphere. Among the basic amines which are employed as liquid anion exchangers the most important are tertiary amines and quaternary ammonium salts (162).

TABLE - I

A LIST OF INORGANIC ION EXCHANGERS PREPARED SO FAR AND THEIR SALIENT FEATURES

Sl. No.	Material	Type of exchanger	Composition	Emperical formula	Selectivity	References
	(I) Aluminium based exchangers					
1.	Aluminium tripoly-phosphate	-	Al/P=0.5-0.66	-	-	(28)
2.	Aluminium anti-monate	Amorphous	Al/Sb = 4.2	-	Ag(I),UO_2(II),Ba(II),Ti(IV)	(29,30)
3.	Aluminium vanadate	Amorphous	-	$(Al_2O_3)_n(V_2O_5)_m$ n/m = 2.0 - 0.5	-	(31)
	(II) Antimony based exchangers					
4.	Antimonic acid	Crystalline	-	$Sb_2O_5.4H_2O$	K(I), Li(I)	(32,33)
5.	Phosphoantimonic acid	Glassy	-	-	Na(I),K(I),NH_4(I),Ag(I)	(34,35)
6.	Phosphorous anti-mony cation exchanger	Amorphous	-	-	-	(36)
7.	Silicon antimony	Amorphous	Sb/Si 3.0 - 5.92 4.48 - 1.81 4.83 - 0.35	-	-	(37)
8.	Antimony ferrocyanide	Amorphous	-	-	Sr(II)	(38)

TABLE-I (Contd.)

Sl. No.	Material	Type of exchanger	Composition	Emperical formula	Selectivity	Reference
9.	Antimony phosphorus silicon	-	-	-	Cd(II),Li(I),Na(I),Mg(II) Sr(II),Ba(II),Y(III), La(III)	(39)
	(III) Bismuth based exchangers					
10.	Bismuth tungstate	Amorphous	Bi/W = 0.5	-	Pb(II)	(40)
11.	Bismuth tellurate	Amorphous	-	$Bi_4(H_4TeO_6)_3 \cdot 9H_2O$	-	(41)
	(IV) Cerium based exchangers					
12.	Cerium phosphate	Amorphous	P/Ce = 1.03-1.95	$Ce_3(OH)_8(H_2PO_4)_4$	Cs(I),Rb(I),K(I) Na(I), Li(I)	(42-45)
		Micro-crystalline	P/Ce = 1.5	$Ce\text{-}O\text{-}Ce(HPO_4)_3 \cdot H_2O$	Cs(I),Na(I),As(I)	
		Crystalline	P/Ce = 2	$Ce(HPO_4)_2 \cdot H_2O$	Pb(II),Ba(II),Ag(I)	(46)
13.	Cerium phosphate sulphate	Crystalline	Ce:P:S 2:1:2	$Ce_2O(HPO_4)_{3-x}(SO_4)_x \cdot 4H_2O$ where $0 < x < 1$	Na(I),Ag(I) Sr(II),Ca(II), Cs(I)	(47)
14.	Cerium arsenate	Micro-crystalline	As/Ce = 2.0	$Ce(HPO_4)_2 \cdot 2H_2O$	-	(48)
15.	Cerium antimonate	Amorphous	Sb/Ce = 0.33	-	Hg(II)	(49)
16.	Cerium molybdate	Amorphous	-	-	-	(50)

TABLE-I (Contd.)

Sl. No.	Material	Type of exchanger	Composition	Emperical formula	Selectivity	References
17.	Cerium tungstate	Amorphous	Ce^{4+}/WO_4^{2-} = 0.49	-	Hg(II), Ti(I)	(51)
18.	Cerium phospho-silicate	Amorphous	Ce:Si:P 2 : 5 : 4	$(CeO_2)_2(SiO_2)_3(H_3PO_4)_4.nH_2O$	-	(52)
	(V) Chromium based exchangers					
19.	Chromium phosphate	Amorphous	P/Cr = 0.6-1.0	$Cr_2O_2HPO_4$ $Cr_2O(HPO_4)_2$	K(I),Na(I),Li(I) Ca(II),Sr(II),Ba(II)	(53) (54)
20.	Chromimum tripoly-phosphate	Glassy	P/Cr = 2.48	$Cr_5(P_3O_{10})_3.nH_2O$	Cs(I),Rb(I),K(I),Na(I)	(53)
21.	Chromium arsenate	Amorphous	As/Cr = 1.98	$Cr_2O_3(H_3AsO_4)_4.3H_2O$	Zr(IV),HF(IV)	(55)
22.	Chromium molybdate	Amorphous	-	$Cr_2O_3(H_2MoO_4)_4.8H_2O$	Pb(II), Ga(III)	(55)
23.	Chromium tungstate	Amorphous	W/Cr = 1.92	$Cr_2O_3(H_2WO_4).11H_2O$	Th(IV), Hf(IV)	(55)
24.	Chromium antimonate	Amorphous	Sb/Cr = 2.95	$Cr_2O_3.3Sb_2O_5.22H_2O$	Pb(II), Co(II)	(55,56)

TABLE-I (Contd.)

Sl. No.	Material	Type of exchanger	Composition	Emperical formula	Selectivity	References
25.	Chromium tellurate	Amorphous	Te/Cr = 0.2	-	-	(57)
26.	Chromium ferrocyanide	Amorphous	Cr/Fe = 0.66	$K_2Cr_2[Fe(CN)_6]_3 \cdot 16\ H_2O$	Cu(II), Ag(I)	(58)
27.	Chromium arsenophosphate	Amorphous	Cr:As:P 2:1:1	$(Cr_2O_3.H_3AsO_4.H_3PO_4).nH_2O$	K(I)	(59)
	(VI) Cobalt based exchangers					
28.	Cobalt antimonate	Amorphous	-	-	-	(60)
29.	Cobalt ferrocyanide	Crystalline	-	-	-	(61)
	(VII) Iron based exchangers					
30.	Ferric phosphate	Amorphous	P/Fe = 2.0	$FeH(HPO_4)_2.nH_2O$	Pb(II), Eu(III), Ga(III)	(62)
31.	Ferric arsenate	Amorphous	As/Fe = 1.33	-	K(I), Na(I), Li(I)	(63)
32.	Ferric antimonate	Amorphous	Sb/Fe = 2.4	-	Cd(II)	(64)
33.	Ferric tungstate	Amorphous	W/Fe = 1.0	-	Ce(IV)	(65)
34.	Ferric ferrocyanide	Amorphous	-	-	Cs(I)	(66)

TABLE-I (Contd.)

Sl. No.	Material	Type of exchanger	Composition	Emperical formula	Selectivity	References
	(VIII) Lead based exchangers					
35.	Lead antimonate	Amorphous	-	-	Pb(II), Cd(II)	(67)
36.	Lead tungstate	Amorphous	-	-	-	(68)
37.	Lead strontium phosphate	-	-	-	-	(69)
	(IX) Magnesium based exchangers					
38.	Magnesium phosphate	Amorphous	-	$Mg_3(PO_4)_2.22H_2O$	-	(70)
39.	Magnesium trisilicate	Amorphous	-	-	-	(71)
	(X) Niobium based exchangers					
40.	Niobium antimonate	Semi-crystalline	Nb/Sb=1.40	$Nb_2.Sb_3.O_{11}(OH)_3.2H_2O$	-	(72)
41.	Niobium arsenate	Amorphous	Nb/As=1.96	-	Rare earth metals	(73)
42.	Niobium molybdate	Amorphous	-	-	La(III)	(74)
43.	Niobium phosphate	Amorphous	-	-	-	(75)
	(XI) Tin based exchangers					
44.	Stannic phosphate	Amorphous	-	-	Na(I),Li(I),Cu(II) Zn(II),Ni(II),Co(II)	(76)
		Crystalline	-	$Sn(HPO_4)_2.H_2O$	-	

TABLE-I (Contd.)

Sl. No.	Material	Type of exchanger	Composition	Emperical formula	Selectivity	References
45.	Stannic arsenate	Amorphous	Sn/As = 1.8	-	Al(III),Ga(III),In(III)	(77)
46.	Stannic antimonate	Amorphous	Sb/Sn = 1.0	-	Cu(II),Ni(II),Co(II)	(78)
47.	Stannic molybdate	Amorphous	Sn/Mo = 1.0	-	Pb(II)	(79)
48.	Stannic selenite	Amorphous	Sn/Se = 1.33 Sn/Se = 1.0	$(SnO_4)(OH)_2(SeO_3).6H_2O$	Li(I),Na(I),K(I) Cu(II),Fe(III),Sc(III)	(80)
49.	Stannic tungstate	Amorphous	Sn/W = 0.33	-	Co(II),Ba(II),Ni(II),Pb(II), Mn(II),Cu(II),Sr(II)	(81)
50.	Stannic vanadate	Amorphous	Sn/V = 1.0	$[(Sn(OH)_3)_3.V_3O_9.4H_2O]_n$	K(I),Na(I),Li(I)	(82)
51.	Stannic ferrocyanide	Amorphous	Sn/Fe = 3.0	$[(SnO)_3(OH)_3.HFe(CN)_6.3H_2O]_n$	K(I),Ba(II),Na(I)	(83)
52.	Stannous ferrocyanide	Amorphous	Sn/Fe = 1.0	$[SnO.H_4Fe(CN)_6.2.5H_2O]_n$	Cu(II),Ni(II),Mg(II), Mn(II), Y(III)	(84)
53.	Stannic arsenophosphate	Amorphous	Sn:As:P 1:1:1	$(SnO_2)_5.(H_3PO_4)_3(H_3AsO_4).nH_2O$	Th(IV),Zr(IV),K(I)	(59)
54.	Stannic molybdoarsenate	Amorphous	Sn:Mo:As 2: 1: 1	-	-	(85)

TABLE-I (Contd.)

Sl. No.	Material	Type of exchanger	Composition	Emperical formula	Selectivity	Reference
55.	Stannic phospho-silicate	Amorphous	Sn:Si:P 2:2:3	$(SnO_2)_2(SiO_2)_2(H_3PO_4).nH_2O$	Hg(II)	(86)
56.	Stannic seleno-phosphate	Amorphous	1:1:1	-	-	(87)
57.	Stannic tungsto-arsenate	Amorphous	Sn:W:As 12:5:2	-	Ba(II),Cu(II)	(88)
58.	Stannic vanado-arsenote	Amorphous	Sn:V:As 1.94:1.14:1	-	Ba(II)	(89)
59.	Stannic vanado-phosphate	Crystalline	-	-	Ba(II),Cu(II)	(90)
60.	Stannic vanado-tungstate	Amorphous	Sn:V:W 2:1:1	-	Al(III)	(91)
	(XII) Tantalum based exchangers					
61.	Tantalum phosphate	Amorphous	-	$TaO_2(H_2PO_4)_{0.88}.6H_2O$	Cs(I),Rb(I)	(92)
62.	Tantalum arsenate	Amorphous	Ta/As=2.8	-	Ba(II),K(I),Na(I)	(93)
63.	Tantalum anti-monate	Amorphous	Ta/Sb = 1.3	-	K(I),NH_4(I),Na(I)	(94)
64.	Tantalum selenite	Amorphous	-	-	-	(95)

TABLE-I (Contd.)

Sl. No.	Material	Type of exchanger	Composition	Emperical formula	Selectivity	References
	(XIII) Titanium based exchangers					
65.	Titanium phosphate	Amorphous	P/Ti = 0.6-2.0	$(TiO)_{0.533}(H_2PO_4)_{0.369}(OH)_{1.77}1.11H_2O$	-	(96,97)
66.	Titanium arsenate	Amorphous	-	$Ti(HAsO_4)_2.2.5H_2O$	Pb(II),Cu(II), Ba(II),Sr(II), Zn(II),Cd(II)	(98)
67.	Titanium antimonate	Amorphous	Sb/Ti = 1.0	-	Rare earth metals	(99)
		Semi-crystalline	-	-	Vo(II)	(100)
68.	Titanium molybdate	Amorphous	Mo/Ti = 0.5-2.0	-	Pb(II),Ba(II),Ti(I), K(I)	(101)
69.	Titanium tungstate	Amorphous	-	-	Cs(I),Mg(II),Ca(II)	(102)
70.	Titanium selenite	Amorphous	Ti/Se = 1.39	-	Cd(II)	(103)
71.	Titanium tellurate	Amorphous	Te/Ti = 2.06	-	-	(57)
72.	Titanium vanadate	Amorphous	V/Ti = 4.0	$Ti(V_3O_9.1.5H_2O)_4 13H_2O$	Sr(II)	(104)
73.	Titanium ferro-cyanide	Amorphous	-	$[TiO_2(OH)HFe(CN)_6.4H_2O]_n$	Cs(I)	(105)
74.	Titanium arseno-phosphate	Amorphous	Ti:As:P 3:1:1	$TiO_2(H_3AsO_4)(H_3PO_4).nH_2O$	-	(106)

TABLE-I (Contd.)

Sl. No.	Material	Type of exchanger	Composition	Emperical formula	Selectivity	References
75.	Titanium molybdophosphate	-	-	-	-	(107)
76.	Titanium phosphosilicate	Amorphous	-	-	Zr(IV),Nb(V),Pu(IV), Cs(I)	(108)
77.	Titanium tungstoarsenate	Amorphous	-	-	Pb(II)	(109)
78.	Titanium tungstophosphate	Amorphous	-	-	Th(IV)	(110)
79.	Titanium vanadophosphate	-	-	-	Rb(I),Cs(I),Ag(I)	(111)
	(XIV) Thorium based exchangers					
80.	Thorium phosphate	Amorphous	P/Th = 1.9-2.1	-	Pb(II),Fe(III),Bi(III)	(112)
		Crystalline	-	$Th(HPO_4)_2.3H_2O$	-	(113)
81.	Thorium arsenate	Crystalline	-	$Th(HAsO_4)_2.H_2O$	-	(114)
82.	Thorium antimonate	Amorphous	Sb:Th=3.67-4.27	-	-	(115)
83.	Thorium molybdate	Amorphous	-	-	Fe(III),Zr(IV),Pb(II)	(116)
84.	Thorium tungstate	Amorphous	Th/W = 2.0	$Th(OH)_2(HWO_4)_2.nH_2O$	Cs(I),K(I),Na(I)	(117)
		Crystalline	-	-	Bi(III),Hg(II)	(118)

TABLE-I (Contd.)

Sl. No.	Material	Type of exchanger	Composition	Emperical formula	Selectivity	References
	(XV) Tungsten based exchangers					
85.	Tungsto antimonic acid	Crystalline	-	-	-	(119)
86.	Tungsten ferrocyanide	Amorphous	W/Fe = 1.32	-	-	(120)
	(XVI) Uranium based exchangers					
87.	Uranyl hydrogen phosphate	-	-	$UO_2HPO_4.4H_2O$	Cs(I),Rb(I),K(I)	(121)
88.	Uranium ferrocyanide	Amorphous	U/Fe = 1.6	-	-	(122)
	(XVII) Zirconium based exchangers					
89.	Zirconium phosphate	Amorphous	P/Zr=0.5-2.1	$Zr(OH)(PO_4)$	Cs(I),Rb(I),K(I),Na(I)	(123)
				$ZrO(HPO_4)$	Eu(III),Sr(II),Co(II),	(124)
				$Zr_3(PO_4)_4$	Ni(II),Zn(II),UO_2(II)	(125)
				$Zr(HPO_4)_2.H_2O$	-	(126)
		Crystalline	P/Zr = 2	$Zr(HPO_4)_2.H_2O$	Na(I),Ag(I),Cs(I),NH_4(I)	(127)
					Sr(II),UO_2(II),Ce(III)	(128)
90.	Zirconium pyrophosphate	Amorphous	P/Zr = 2.0, 2.5 - 2.8	-	Cu(II),Ni(II),Ca(II), Na(I),Fe(II),Mg(II)	(129)
91.	Zirconium hypophosphate	Amorphous	P/Zr = 1.57	-	For multivalent metals	(130)

TABLE-I (Contd.)

Sl. No.	Material	Type of exchanger	Composition	Emperical formula	Selectivity	References
92.	Zirconium polyphosphate	Amorphous	-	-	For alkali metals (in NH_4(I) form) and Fe(III),Cu(II),Ca(II), Ba(II) (in H(I) form)	(131,132
93.	Zirconium arsenate	Amorphous	As/Zr= 1.53-1.96	-	Cs(I),K(I),Na(I)	(133)
		Crystalline	As/Zr = 2	$Zr(HAsO_4)_2.H_2O$	Na(I),K(I),Cs(I)	(133)
94.	Zirconium intimonate	Amorphous	-	-	Na(I),K(I),NH_4(I),Rb(I)	(134)
					Cs(I), Li(I)	(135)
95.	Zirconium molybdate	Amorphous	Zr/Mo= 8.5 - 2.0	-	-	(136)
96.	Zirconium tungstate	Amorphous	Zr/W = 1.0-0.44	-	Cs(I),Rb(I),K(I), Na(I),Li(I),Hg(II)	(137,138)
97.	Zirconium tellurate	Amorphous	-	$Zr(H_2TeO_6).H_2O$	-	(139)
98.	Zirconium oxalate	Crystalline	-	$Zr(OH)C_2O_4H$	Na(I),Cs(I),Rb(I),K(I)	(140)
99.	Zirconium silicate	Amorphous	-	-	Th(IV),Sm(III),Ca(II), Sr(II)	(141,142)
100.	Zirconium ferrocyanide	Amorphous	Fe/Zr= 0.55	-	Li(I),Na(I),NH_4(I)	(143)

TABLE-I (Contd.)

Sl. No.	Material	Type of exchanger	Composition	Emperical formula	Selectivity	References
101.	Zirconium arseno-phosphate	Amorphous	Zr:As:P 2:1:1	$(ZrO_2)(H_3AsO_4)(H_3PO_4).nH_2O$	-	(144)
102.	Zirconium arseno-phosphate	Amorphous	1:2:1	$2ZrO_2.2As_2O_5.10H_2O$	-	(145)
103.	Zirconium tungsto-arsenate	-	-	-	Ag(I)	(146)
104.	Zirconium titanium-phosphate	Crystalline	-	-	-	(147)
105.	Zirconium alumino-pyrophosphate	-	-	-	-	(148)
106.	Zirconium arseno-silicate	Crystalline	Zr:As:Si 1:2:1	-	Al(III),Fe(III), Pb(II),Cd(II)	(149)
107.	Zirconium molybdo-vanadate	-	Zr:V:Mo 1.68:1.00:0.088 3.33:1.00:0.28 6.15:1.00:0.815	-	Li(I),Na(I)	(150)
108.	Zirconium molybdo-phosphate	-	-	$ZrH_2MoO_{12}.nH_2O$	-	(107)
109.	Zirconium phospho-silicate	Amorphous	-	-	Pu(IV),Cs(I)	(151)

TABLE-I (Contd.)

Sl. No.	Material	Type of exchanger	Composition	Emperical formula	Selectivity	References
110.	Zirconium phospho-iodate	Electron ion-exchanger	-	-	Qualitative oxidation of Fe(II),Ti(III), As(III),Sn(II),Sb(III)	(152)
	(XVIII) Other acidic salts					
111.	Cesium zirconium phosphate	-	-	-	-	(153)
112.	Collidinium molybdo-arsenate	-	-	-	Tl(I),La(III)	(154)
113.	Hafnium phosphate	Amorphous	-	-	Li(I)	(155)
114.	Lanthanum antimo-nate	Amorphous	-	-	Hg(II),Mg(II)	(156)
115.	Molybdate ferro-cyanide	Semi-crystalline	Fe/Mo = 2.3	$\left[H_4Fe(CN)_6\right]_4 (MoO_3(H_2O)_n)_{16}$	Cs(I)	(157)
116.	Nickel antimonate	Amorphous	-	-	Bi(III)	(60)
117.	Pyridinium tungsto-arsenate	-	-	-	Rb(I),Cs(I)	(158)
118.	Tellurium antimony	Amorphous	Sb/Te = 1.93-6.23	-	-	(159)

TABLE-I (Contd.)

Sl. No.	Material	Type of exchanger	Composition	Emperical formula	Selectivity	References
119.	Vanadium ferro-cyanide	Amorphous	V/Fe = 3.86	-	Cs(I),Rb(I)	(160)
120.	Zinc ferro-cyanide	Amorphous	Zn/Fe = 1.98	$Zn_2Fe(CN)_6$	Cs(I)	(161)

Ion chromatography, which uses resins whose ion exchange function resides in a thin surface film, is now very popular (163-167). The method is especially useful for anions, and very low concentrations can be measured, down to parts perbillion if concentrator columns are used (168). In its orthodox form, ion chromatography depends on conductometric detection, preceded by a "Supressor Column" to remove ions of the eluent. The supressor column can be eliminated if a suitable ion-selective detector is used (169).

A new aspect of ion exchange is the wide spread use of paired-ion chromatography, in which the stationary phase is hydrophobic packing and the mobile phase contains long chain, hydrophobic ions of opposite charge to the ions being separated. Paired-ion chromatography, developed for organic ions, has now been used for inorganic species like halides, azide ions and oxy anions of nitrogen, sulphur, and the halogens (170).

In order to understand the mechanism of an ion exchange process, it is important to have a study of its kinetics and thermodynamics. Since inorganic ion exchangers possess a rigid matrix they do not swell appreciably and hence such studies are simpler to perform on them as compared to the organic resins which swell appreciably. An ion exchange equilibrium may be described by two theoretical approaches viz. (a) based on the law of mass action, and (b) based on the Donnan theory. From the theoretical point of view the

Donnan theory has an advantage of permitting a more elegant interpretation of the thermodynamic behaviour in an ion-exchanger. However, from the practical point of view, the mass action approach is simpler. Many workers have studied the thermodynamics of cation exchange on zirconium (IV) phosphate (171-174). Nancollas and Co-workers (175,176) have interpreted the thermodynamical functions in terms of the binding nature between alkali metals and the ion exchanger matrix. The ion exchange equilibria of Li(I), Na(I) and K(I) on zirconium (IV) phosphate have also been studied by Larsen and Vissers (177) who calculated the equilibrium constants and other thermodynamical parameters viz. ΔG^{o}, ΔH^{o} and ΔS^{o}. Similar studies have been made on anion exchangers also (178).

Nachod and Wood (179) have made the first serious and detailed attempt on the kinetic studies of ion exchange. They have studied the reaction rate with which ions from solutions are removed by the solid ion exchangers or conversely the rate with which the exchangeable ions are released from the exchanger. Later on, Boyed et al. (180) have studied the kinetics of metal ions upon the resin beads and have given a clear understanding about the particle and film diffusion phenomena which govern the ion exchange processes. The former is valid at higher concentrations while the latter at the lower ones. The kinetics of metal ions on sulphonated polystyrene has been studied by Reichenberg (181) who again confirmed that at high concentrations the rate is independent of the in-

going ion (particle diffusion), while at low concentrations the reverse is true (film diffusion). According to Nancollas (182) who studied the kinetics of Na(I) - H(I) exchange on crystalline zirconium phosphate, the rate of exchange is initially fast and then becomes slow. Fuga and Kikindi (183) have studied the kinetics of ion exchange of alkali metals on zirconium antimonate in hydrogen form at 25°C and have found that the rate of reaction increases with the atomic number of the cation. Alberti et al. (184) have observed that the rate of exchange decreases from Ba(II) to Sr(II) and that it is particularly low for Mg(II) ion on zirconium(IV) phosphate. Recently, costantino (185) has studied the self-diffusion of Na(I) and K(I) on microcrystals of $Zr(NaPO_4)_2.3H_2O$ and $Zr(KPO_4).3H_2O$ and has modified the Fick's equation to take into account the non-uniformity of the particle size. The equation obtained has been employed in a study of the self-diffusion rate of Na(I) and K(I) in the above exchangers and the mobility data have been compared with the conductivity data available for the same ionic forms.

The studies made so far in the field of inorganic ion exchangers point to the following interesting conclusions:

1. They show in general a poor reproducibility in their behaviour.
2. Their stability is not, generally very high.
3. A very little effort has been made regarding their kinetic and thermodynamic studies, which are important to understand the mechanism of ion exchange.

4. The claim that they are highly stable under strong radiations and at elevated temperatures, appears to be an over emphesized one because only rare studies have actually been carried out in these directions supporting this view.

In view of the above, the present study is aimed to synthesize antimony (V) silicate a new material possessing satisfactory stability and crystalline nature and to understand the mechanism of ion exchange on its surface by applying the kinetic and thermodynamic approaches. Finally, its utility has been demonstrated by achieving some analytically important separations on its columns.

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CHAPTER - II

SYNTHESIS, ION EXCHANGE BEHAVIOUR AND STABILITY OF A CRYSTALLINE ANTIMONY(V) SILICATE CATION EXCHANGER

A large number of inorganic materials possessing ion exchange properties have been synthesized and used for various separations of analytical and radiochemical importance (1-5). They are of growing interest in relation to the treatment of contaminated water or coolant moderator in reactors working at high temperature and pressure (1), as it is generally believed that they are resistant for heat and radiations. However, very few reports (5-8) have appeared in the literature confirming this belief. Zsinka et al. (9) have reported that a generalization about the resistance of inorganic ion exchangers against radiations can not be made, and supported by Tandon et al. (10).

Hydrous oxides of some quinique and sexivalent metals such as Nb, Ta, Sb(V), Mo(V), and W(VI) exhibit cation exchange properties(11). Among them hydrous antimony(V) oxide (so called antimonic acid or polyantimonic acid) has been the most intensively studied, owing to its high exchange capacity, a reasonable rate of exchange and desorption, and high selectivities for certain elements. In 1923, Jander and Simon (12) reported that antimonic (V) acid adsorbed lithium ions from a dilute lithium sulphate solution, giving an amorphous mass of indefinite composition. In recent years Abe and Ito (13-15) and Lefebvre (16) have reported that the adsorption and desorption of potassium ions on antimonic

acid is due to an ion exchange on its surface. Lefebvre and Gaymard (17) have also reported that the adsorption of alkali and alkaline earth metals on antimonic acid is governed by an ion exchange mechanism with a selectivity sequence in the order:

$$Na(I) > K(I) > NH_4(I) > Rb(I) > Cs(I) \text{ and}$$
$$Ba(II) > Sr(II) > Ca(II) > Mg(II).$$

Baetsle et al. (18,19) have also reported that polyantimonic acid shows promise for ^{90}Sr and ^{137}Cs recovery from acid reprocessing effluents. The adsorption properties of antimonic cation exchangers depend on their preparative conditions, e.g., aging, drying conditions etc. Crystalline antimonic acid shows extremely high values of distribution coefficients for Na(I) (20), Sr(II) (21), Cd(II) (22), and Hg(II) (23).

Silicates are known to form one of the most important classes of the ion exchange materials as they are temperature resistant and stable under chemical attack (24-27). Antimony salts such as Zr(IV), Ti(IV), and Sn(IV) antimonates (28-31) have received attention because of their reproducible ion exchange behaviour while the antimony-silicon cation exchangers have been prepared and studied by Nooikov and co-workers (32-36). However antimony(V) silicate has not received a proper attention as an ion exchanger. The present study is, therefore, aimed to prepare a crystalline sample of this material and to perform a systematic study of its ion exchange behaviour.

EXPERIMENTAL

Reagents

Antimony pentachloride used in this study was of ~95% purity obtained from KOCh-Light Laboratories Ltd. (Colnbrook, Bucks, England) and the sodium silicate was a Riedal (DEHAENAG, Seelze-Hannover) product. All other reagents and chemicals were of AnalaR grade.

Apparatus

pH-measurements were made on an Elico (India) model LI-10 ph meter while infrared studies were performed on a Beckmann IR-20 spectrophotometer. X-ray studies were made on a philips X-ray unit using a Mo-Kα Target of wave length 0.7107A°, and the radioactivity was measured in a well type single channel counter of the Electronics corporation of India Ltd. using a NaI(Tl) detector. Thermogravimetric studies were performed on a Modern TGA balance of the Fertilizers corporation of India (Ltd.). A Bausch and Lomb Spectronic-20 colorimeter was used for the spectrophotometric studies.

Preparation of the reagent solutions

A stock solution (1.0M) of antimony penta chloride ($SbCl_5$) was prepared in a 4.0M HCl solution. Further dilutions to the

desired concentrations were also made by 4M HCl. Sodium silicate ($Na_2SiO_3.3H_2O$) was dissolved directly in demineralized water (DMW).

Synthesis of the ion exchange material

Various samples of antimony(V) silicate (SbSi) were prepared by varying the concentration of the mixing solutions as given in Table-II and the pH of the resulting gel was fixed in the range 0-1, by adding sodium hydroxide with constant stirring. The gel thus obtained was kept for 24 hours at room temperature ($\sim 30^{\circ}C$) and filtered by suction. The excess acid was removed by washing with DMW and the material was dried in an air oven at $45^{\circ}C$. It was then cracked into small granules by putting in DMW, and the granules so obtained were of the uniform size suitable for column operations. The particles of a uniform mesh size were obtained by seiving and were converted into the H^+ form by treating with 1M HNO_3 for 24 hours with occasional shaking, intermittently replacing the supernatant liquid with a fresh acid. The material thus obtained was finally washed to remove the excess acid and then dried at $45^{\circ}C$. The exchanger beads are thus ready for further studies. On the basis of its apparent chemical stability, appearence and Na^+ ion exchange capacity, sample S-6 was selected for all the studies. The reproducibility was checked by preparing the samples several times following the same procedure.

TABLE - II

SYNTHESIS OF VARIOUS SAMPLES OF ANTIMONY(V) SILICATE AS AN ION EXCHANGE MATERIAL

Sample No.	Concentration of mixing solutions(M) ($SbCl_5$+$Na_2SiO_3.3H_2O$)	Mixing ratio (Sb : Si) by volume	Na^+ Ion exchange capacity (meq/g)
S-1	0.5	1:1	Unstable in solution
S-2	0.4	1:1	1.6
S-3	0.3	1:1	1.7
S-4	0.2	1:1	1.5
S-5	0.1	1:1	1.7
S-6	0.1	2:1	1.6

Composition

Antimony and silica present in the exchanger were determined by the following procedures:

Determination of antimony

250 mg of the powdered exchanger were fused with 4g Na_2CO_3 and transferred in a beaker containing 100 ml solution of 4M HCl. Antimony was determined volumetrically in this solution with $KBrO_3$, using methyl orange as an indicator (37).

Determination of silica

250 mg of the powdered exchanger were fused with ~ 4g of Na_2CO_3 in a platinum crucible and transferred in a ~ 75 ml solution of 4M HCl in a beaker. The volume was reduced by evaporation and then subjected to the desication process. The undissociated silica was filtered through a whatman No. 540 paper and washed with 4M HCl. The filtrate was again subjected to the desication process, and the residue filtered and washed. The combined residue was ignited on a platinum crucible and weighed (38).

The results are summarized in Table III.

TABLE - III

COMPOSITION OF ANTIMONY(V) SILICATE

Sl. No.	Weight of the exchanger	Millimoles of the components		Mole ratio
		Antimony	Silicon	
1.	250	0.56	1.68	1:3.00
2.	250	0.65	2.00	1:3.07
3.	250	0.66	2.01	1:3.04

Chemical stability

The solubility of antimony(V) silicate in various solvents was determined as given below:

250 mg portions of the material were kept with 25 ml of the solvent for 24 hours at room temperature with intermittent shaking. Antimony and silicon were determined quantitatively in the supernatant liquid as follows:

(a) Determination of antimony

To the 2 ml portion of the above solution were added 1.6 ml of 18N H_2SO_4 and 5 ml of KI reagent (11.2g of KI + 2g of ascorbic acid in 100 ml water). The colour so developed was diluted to 10 ml with water in a standard volumetric flask and the absorbance was measured after 2-3 minutes at 425 mμ against a reagent blank (39).

(b) Determination of silicon

5 ml of the supernatent liquid was mixed with 0.2 ml of 10% ammonium molybdate and 2 drops of 50% H_2SO_4 solutions. The colour so developed was diluted to 10 ml with water in a standard volumetric flask, and the absorbance was measured immediately at 420 mμ against a reagent blank (40). Table IV summarizes the results.

TABLE-IV

CHEMICAL STABILITY OF ANTIMONY(V) SILICATE IN VARIOUS ACID, ALKALI AND SALT SOLUTIONS.

Solvent (25 ml)	Amount dissolved in mg	
	Antimony	Silicon
1M HNO_3	0.65	0.00
2M HNO_3	2.34	0.00
4M HNO_3	2.95	0.07
1M HCl	1.31	0.00
2M HCl	1.40	0.00
4M HCl	5.51	0.00
1M H_2SO_4	1.68	0.00
4M H_2SO_4	3.50	0.00
2M $NaNO_3$	0.00	0.00
2M KNO_3	0.09	1.55
0.05M NaOH	4.58	3.50
0.1M NaOH	Dissolved appreciably	Dissolved appreciably
0.1M KOH	Dissolved appreciably	Dissolved appreciably
0.1M NH_4OH	1.68	3.15
0.5M NH_4OH	4.44	1.20

Ion exchange capacity (i.e.c.)

The i.e.c. was determined as usual by the column process taking 1g of the exchanger (H^+ form) in a glass tube of i.d.~ 1 cm, fitted with the glass wool at its bottom, and maintaining a very slow flow rate (~ 0.5 ml/min.). The total volume of the eluant necessary for the complete elution of H^+ ions was 250 ml. The effluent was titrated against a standard alkali solution to find out the total H^+ ions eluted. Table V summarizes the values of i.e.c. for various metal ions.

Effect of eluant concentration on the i.e.c.

The extent of elution was found to depend upon the concentration of the eluant. Hence a fixed volume (125 ml) of the $NaNO_3$ solution of varying concentrations was passed through the column containing 0.5 g of the exchanger and the effluent was titrated against a standard alkali solution for the H^+ ions eluted out. Figure 1 shows the variation of the H^+ ions eluted out with the concentration of the eluant.

Elution behaviour

The column containing 1 g of the material in H^+ form was eluted with a 1M $NaNO_3$ solution having the standard flow rate and several 10 ml fractions of the effluent were collected and titrated for the H^+ ions released. The total volume was fixed as 250 ml. Figure 2 shows the elution behaviour of the exchanger.

TABLE-V

ION EXCHANGE CAPACITY OF ANTIMONY(V) SILICATE FOR VARIOUS METAL SOLUTIONS.

Metal Solutions	Ion exchange Capacity (meq / dry g)
LiCl	1.05
$NaNO_3$	1.60
KCl	1.49
$Mg(NO_3)_2$	1.53
$Ca(NO_3)_2$	1.10
$Sr(NO_3)_2$	1.59
$BaCl_2$	1.61
NH_4NO_3	0.8

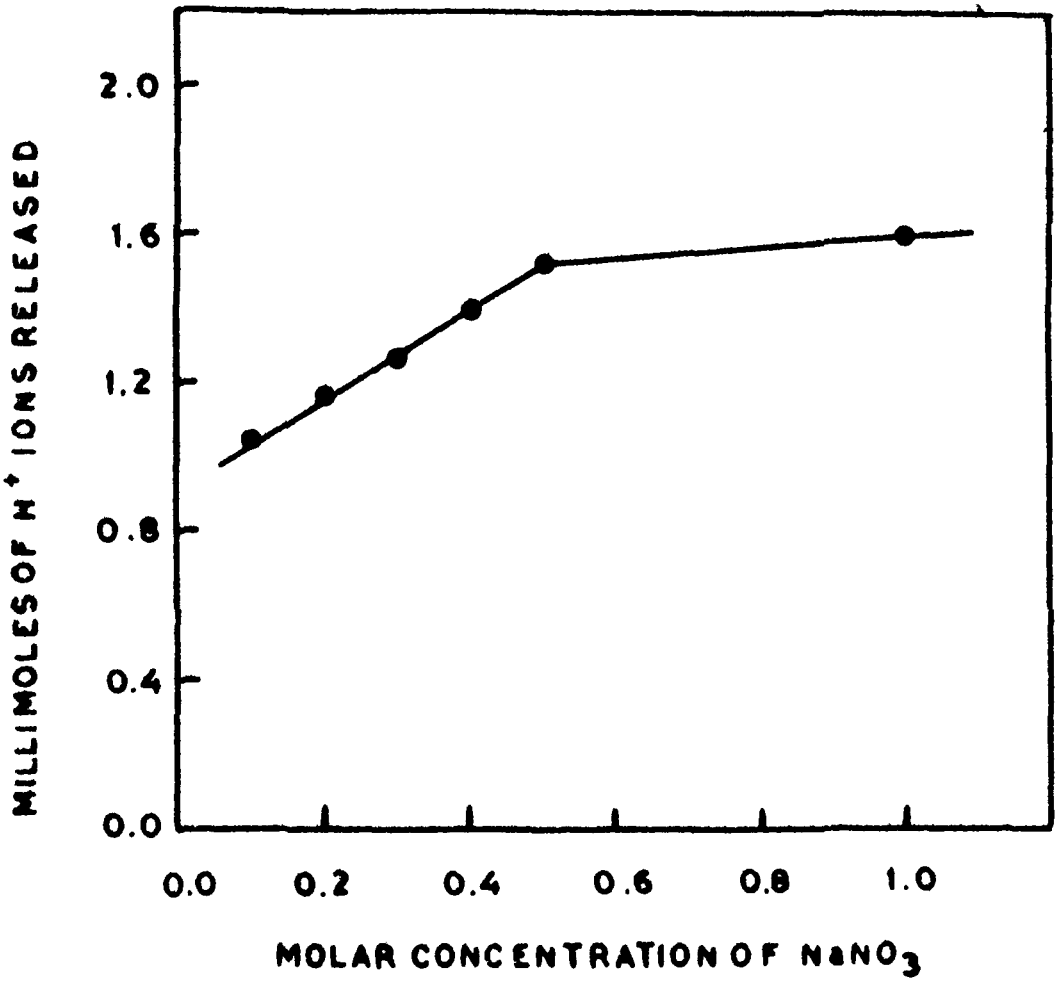

FIG. 1 CONCENTRATION PLOT OF ANTIMONY(V)SILICATE CATION EXCHANGER

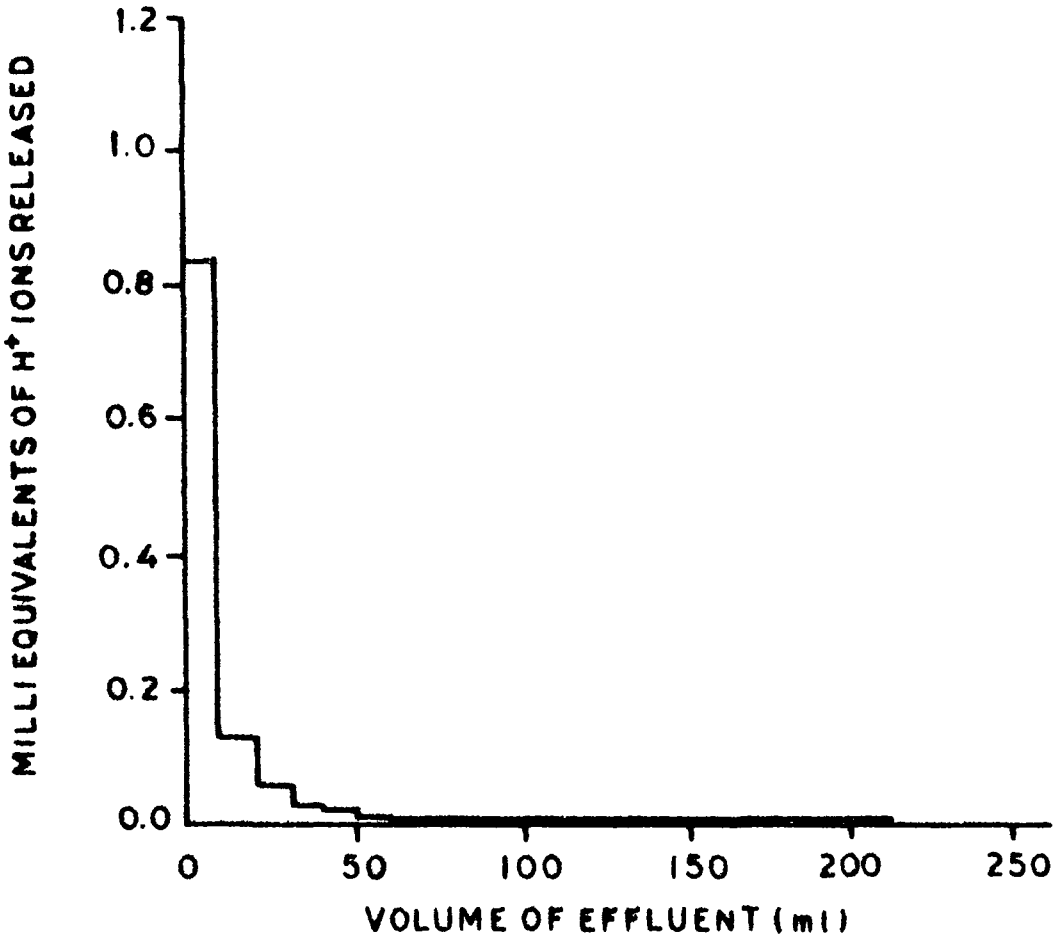

FIG. 2 HISTOGRAMS SHOWING THE ELUTION BEHAVIOUR OF ANTIMONY (V)SILICATE CATION EXCHANGER

pH titrations

pH titrations were performed by the method of Topp and Pepper (41), 500 mg of the exchanger were placed in each of the several 250 ml conical flasks, followed by the equimolar solutions of alkali metal chlorides and their hydroxide in different volume ratios, the final volume being 50 ml to maintain the ionic strength constant. The pH of the solution was recorded after equilibrium and was plotted against the milliequivalents of the OH^- ions added as shown in Figure 3.

Thermal stability

Several 1 g portions of the sample S-6 were heated at various temperatures in a muffle furnace for 1 hour each, and the i.e.c. was determined as above by the column process after cooling them to the room temperature. It was also determined after heating the material for 4 hours at 400° and 800°C. The results are shown in Table VI.

Thermogravimetric analysis (TGA)

It was done by an automatic thermobalance which recorded the weight loss on heating the material at a constant rate (10° C/min). Figure 4 shows the percent weight loss occurred on heating the sample upto 600°C.

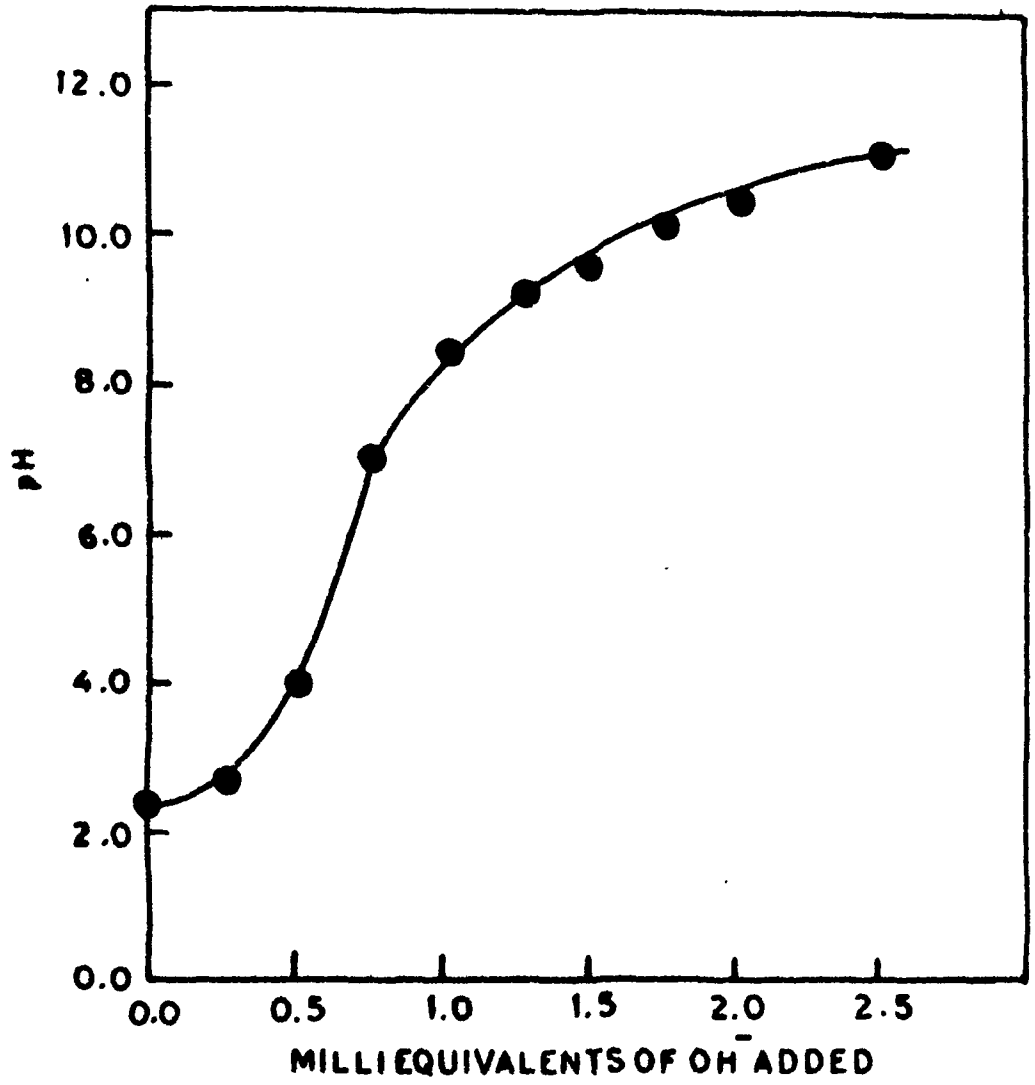

FIG. 3 pH TITRATION CURVE OF ANTIMONY(V)SILICATE

TABLE - VI

ION EXCHANGE CAPACITY AND APPEARANCE OF ANTIMONY(V) SILICATE AFTER HEATING TO VARIOUS TEMPERATURES.

Drying temperature in ^{o}C	Time of heating	Na^{+}-ion exchange capacity (meq / dry g)	Appearance
45	1 hour	1.6	White
100	1 hour	1.52	White
300	1 hour	1.42	Yellowish white
400	1 hour	1.25	Yellowish white
600	1 hour	1.20	Dark yellow
800	1 hour	0.72	Yellowish white
400	4 hours	1.18	Yellowish white
800	4 hours	0.34	Yellowish white

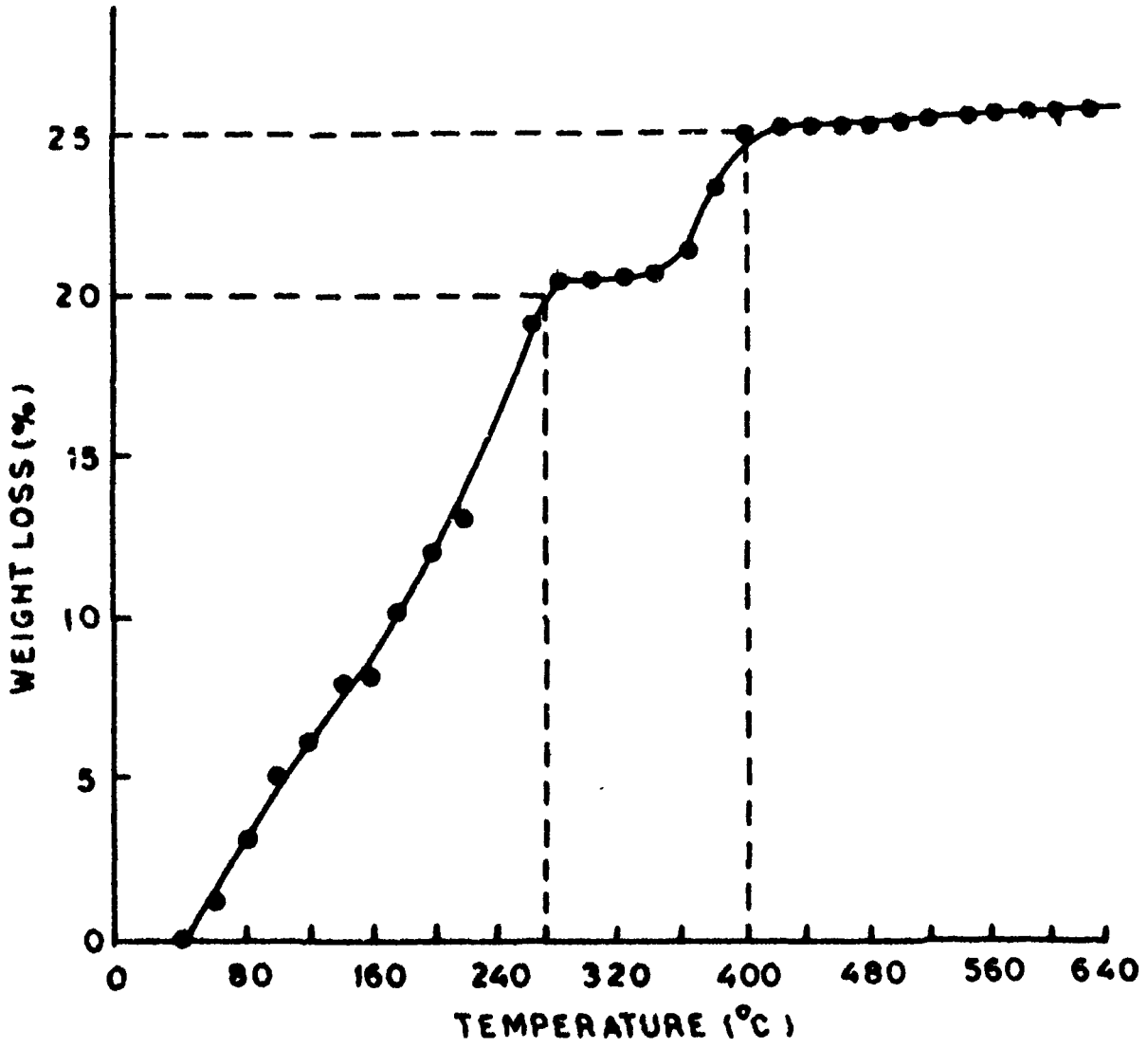

FIG. 4 THERMOGRAM OF ANTIMONY (V) SILICATE CATION EXCHANGER

IR Studies

The IR spectra of antimony(V) silicate in H^+ form were taken by the KBr Disc method as shown in Figure 5, which also includes the IR spectra of the SbSi heated at 400°C for 1 hour and 4 hours.

X-ray Studies

Figure 6 gives the X-ray diffraction patterns of the SbSi samples obtained on heating to various temperatures. Table VII summarizes the results of these studies. The lattice constant (a) was determined by the formula:

$$a^2 = \frac{\lambda^2(h^2 + k^2 + l^2)}{4 \sin^2 \theta}$$

where λ is the wave length of the incident beam and h,k,l are the plane indices.

Radiation stability

Antimony(V) silicate in H^+ form was irradiated by the gamma rays at a dose rate of 0.4M rads/hour using ^{60}Co as a source and $FeSO_4$ as a dosimeter to give the total dose as 1×10^8, 2×10^8 and 3×10^8 rads. The changes in the various properties of the material are given in Table VIII. Figures 7, 8 and 9 illustrate the effect of gamma irradiation on the elution behaviour, pH-titrations and IR spectra of the material. A comparison of the irradiation effect on the ion exchange capacity of various inorganic ion exchangers with antimony(V) silicate is given in Figure 10.

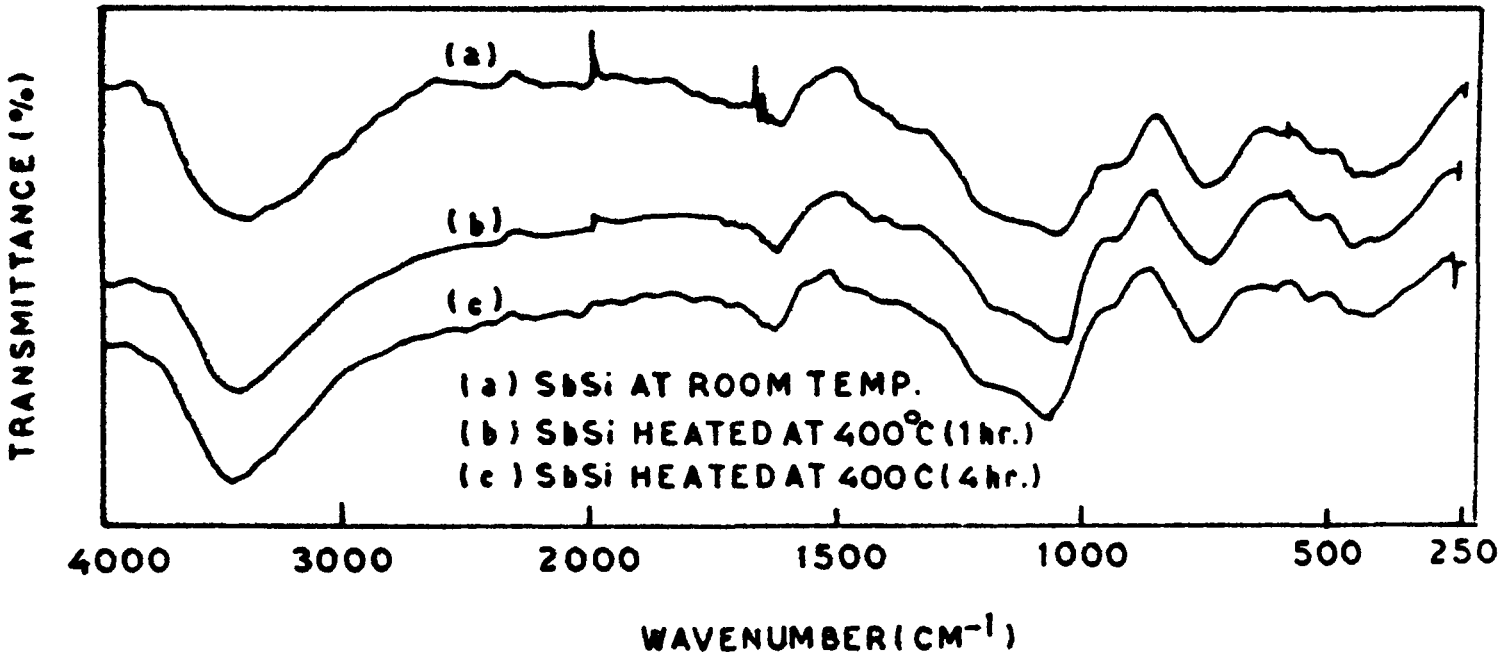

FIG. 5 I.R. SPECTRA OF SOME SAMPLES OF ANTIMONY (V) SILICATE CATION EXCHANGER

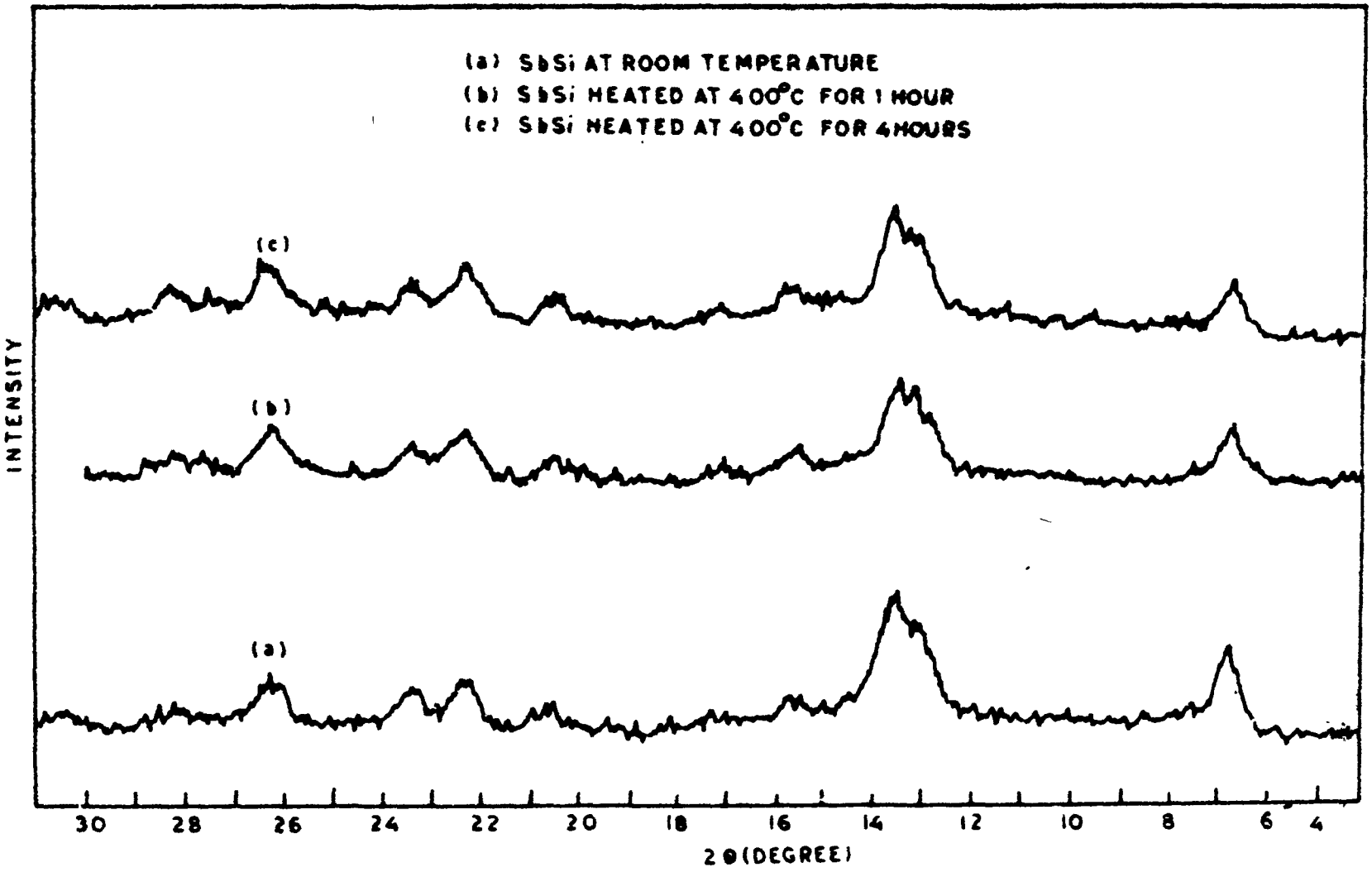

FIG. 6 X-RAY DIFFRACTION PATTERNS OF ANTIMONY(V)SILICATE CATION EXCHANGER

TABLE - VII

X-RAY POWDER DIFFRACTION DATA FOR CRYSTALLINE ANTIMONY(V) SILICATE

Sl. No.	2 θ	Relative Intensity (in a scale of 100)	θ	Sin θ	2Sin θ	d (A^{o}) ($\frac{n\lambda}{2\sin\theta}$)	$\sin^2\theta$	Indices (hkl) (Error)
1.	6.75	55	3.375	0.05887	0.11774	6.0362	0.00347	110 (0.0000)
2.	13.44	100	6.720	0.11702	0.23404	3.03666	0.01369	220 (0.0002)
3.	15.30	30	7.650	0.13355	0.26624	2.66940	0.01772	310 (0.0004)
4.	20.30	25	10.150	0.17623	0.35246	2.01640	0.03106	411,330 (0.0001)
5.	22.40	30	11.200	0.19423	0.38846	1.8295	0.03773	332 (0.0004)
6.	23.45	30	11.725	0.20321	0.40642	1.74868	0.04129	422 (0.0003)
7.	26.25	40	13.125	0.22700	0.45400	1.56541	0.05153	521 (0.0005)
8.	28.20	25	14.100	0.24362	0.48724	1.45862	0.05935	530 (0.0003)

The avarage lattice constant, a = 8.543 A^{o}

TABLE - VIII

EFFECT OF IRRADIATION ON CERTAIN PHYSICAL AND ION EXCHANGE PROPERTIES OF ANTIMONY(V) SILICATE.

Sl. No.	Ion exchange property	Observations
1.	Appearance	No change
2.	Colour	No change
3.	Grain size	No change
4.	Brittleness	No change
5.	Ion exchange capacity	No change
6.	pH titration	No change
7.	Elution behaviour	Slight decrease in the elution rate.
8.	IR spectrum	No significant change.

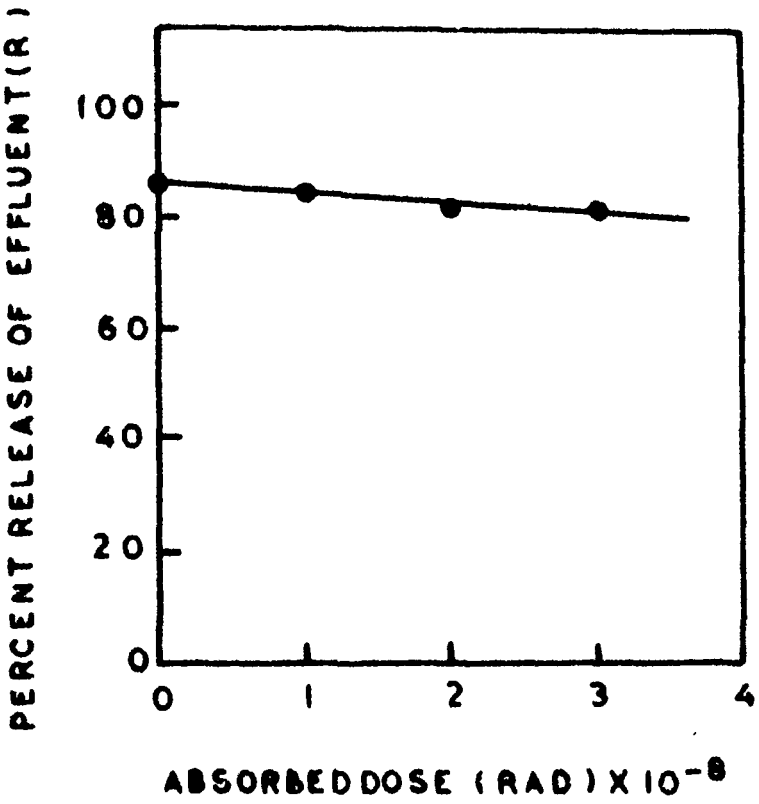

FIG. 7 EFFECT OF GAMMA RADIATIONS ON THE ELUTION BEHAVIOUR OF ANTIMONY(V)SILICATE

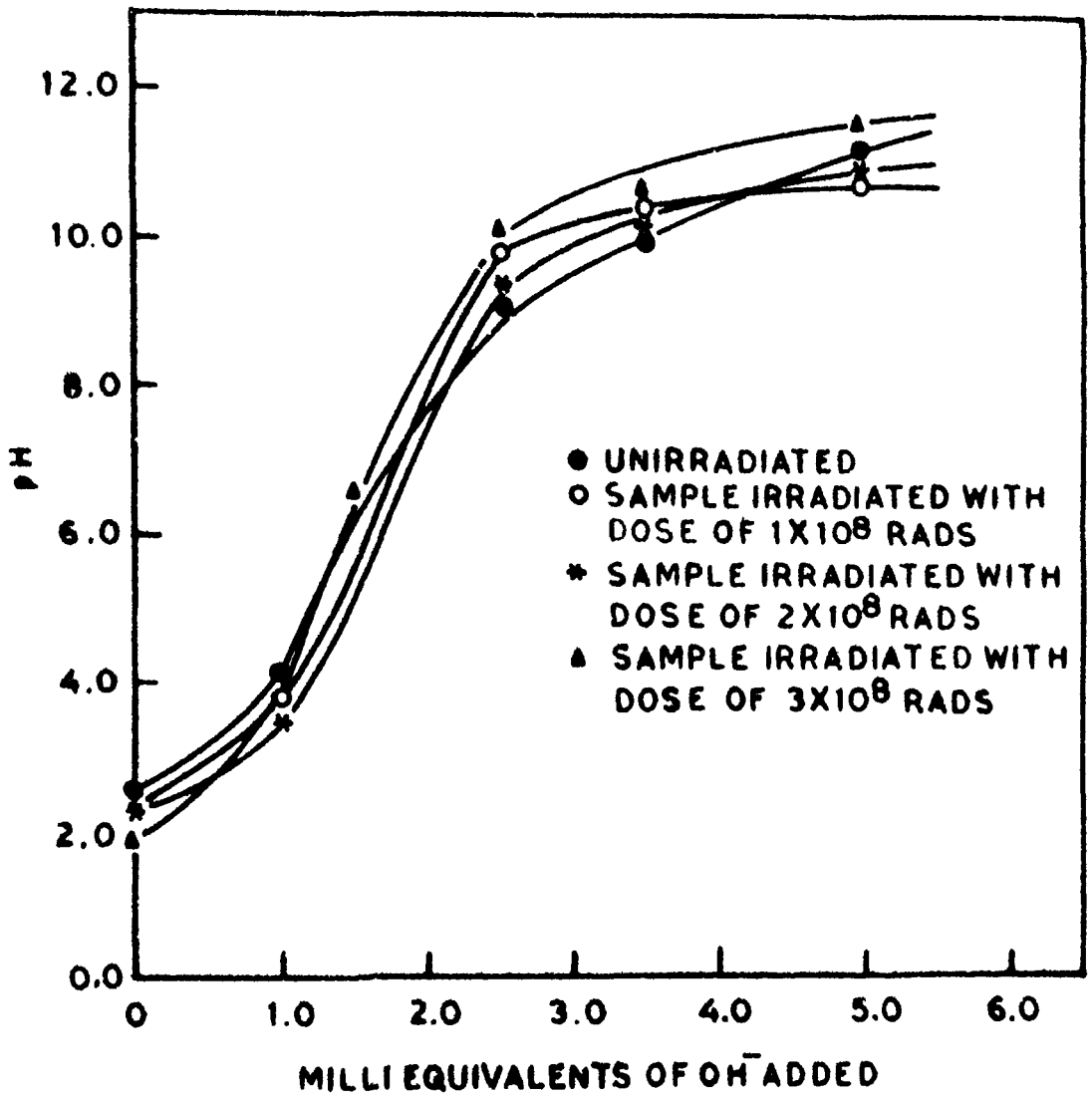

FIG. 8 EFFECT OF GAMMA RADIATIONS ON THE pH TITRATIONS OF ANTIMONY (V) SILICATE CATION EXCHANGER

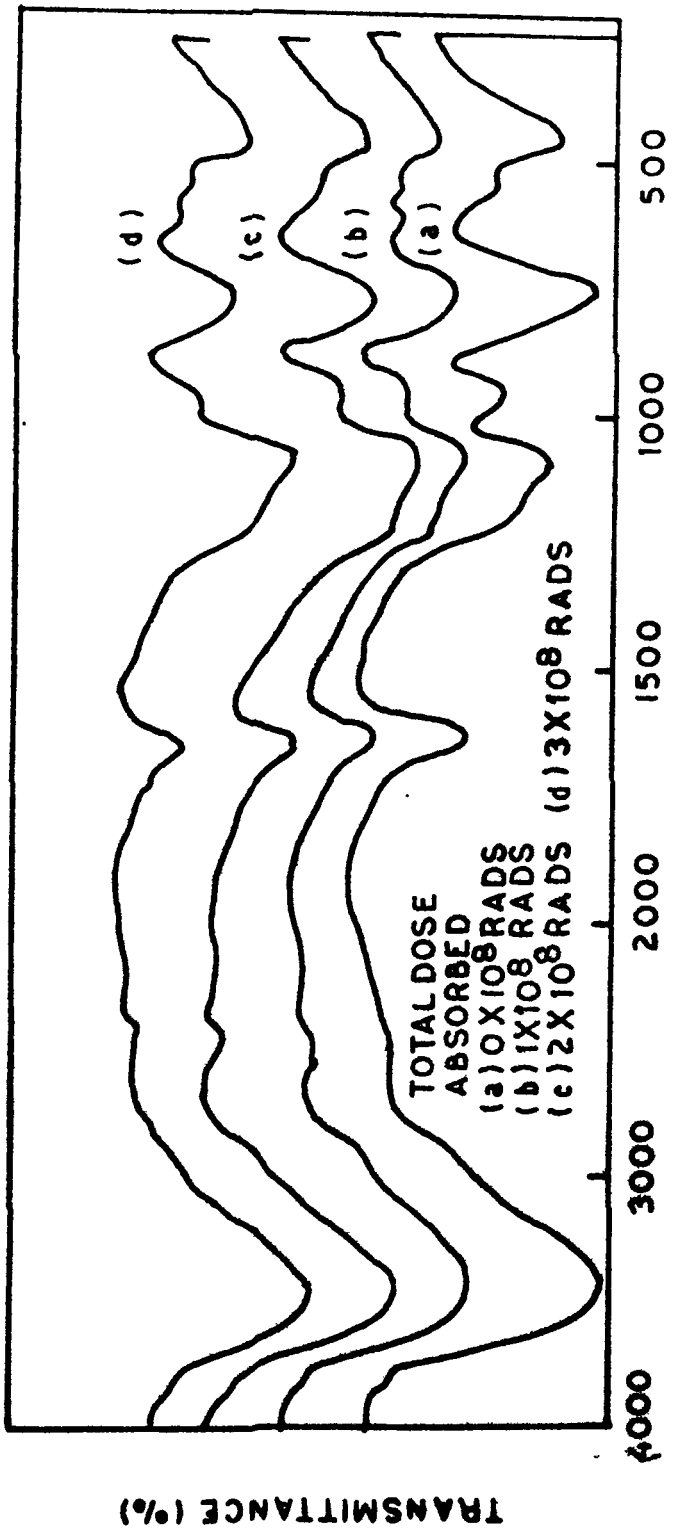

FIG. 9 I.R. SPECTRA OF VARIOUS IRRADIATED AND UNIRRADIATED SAMPLES OF ANTIMONY (V) SILICATE

DISCUSSION

Antimony(V) silicate (SbSi) prepared in these studies shows a cation exchange capacity comparable with other materials of this class and illustrates a high reproducibility in its ion exchange behaviour. It shows a high chemical, thermal and radiation stability. As it is clear from Figure 11 antimony(V) silicate retains $\sim$ 75% of its i.e.c. even on heating upto 600°C for an hour, which is comparable with other inorganic ion exchangers such as zirconium arsenophosphate, titanium arsenophosphate (26) and cerium phosphosilicate (27) prepared earlier when the material was heated to various temperatures (45° to 800°C), it was observed that a heating upto 400°C does not alter its ion exchange capacity (Table VI). It is a peculiar and unusual behaviour of this material..

The elution studies indicate that the exchange is quite fast and almost all the H^+ ions are leached out of the column within the first 50 ml of the effluent (Figure 2). Moreover, the exchange takes place in one step as indicated by the pH titration curve (Figure 3).

The irradiation studies reveal that the material is highly resistant to gamma radiations (Table VIII). Organic resins undergo $\sim$ 15% loss in their i.e.c. on such a treatment (7). pH titra-

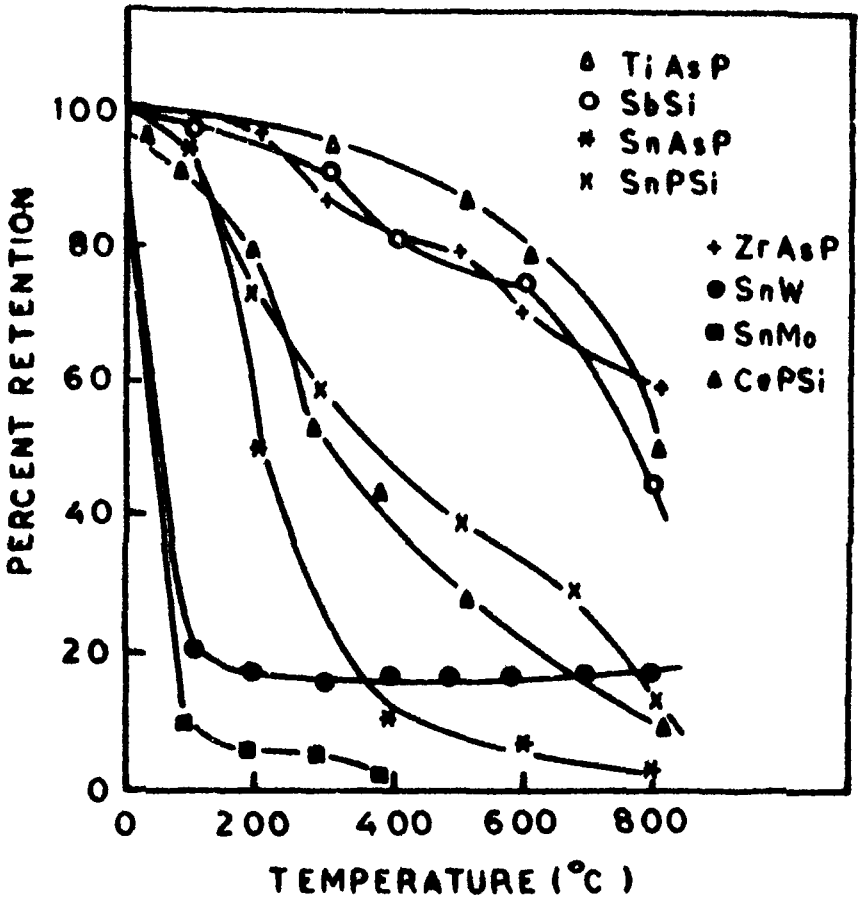

FIG. 11 PERCENT RETENTION IN THE ION EXCHANGE CAPACITY OF ANTIMONY (V) SILICATE AND ITS COMPARISON WITH SOME INORGANIC ION EXCHANGERS ON HEATING

tion curves (Figure 8) and IR spectra (Figure 9) do not indicate any significant structural changes after irradiation even upto the total dose of 3×10^8 rads.

The IR spectra (Figure 5) show several peaks at $\sim$ 450, $\sim$ 750, $\sim$ 1050, $\sim$ 1600 and $\sim$ 3300 cm^{-1}. The peaks observed at $\sim$ 450 and $\sim$ 750 cm^{-1} are indicative of the metal-oxygen stretching vibrations while those appeared at $\sim$ 1050 are due to the presence of silicate (42). The presence of water of crystallization is indicated by the peaks at $\sim$ 1600 and $\sim$ 300 cm^{-1}. The peaks at $\sim$ 1600 cm^{-1} are also indicative of the strongly hydrogen bonded OH or extremely strongly coordinated H_2O. On heating the exchanger upto 400°C for 4 hours the peaks at $\sim$ 1600 cm^{-1} are broadened and become less intensive probably because of the removal of the interstitial water molecules from the structure.

The X-ray diffraction pattern (Figure 6) reveals that the material is crystalline. The nature of crystallinity does not change significantly (such as signal position and width of the peaks) even after heating the exchanger to 400°C for 4 hours. As it is clear from Table VII the crystals of antimony(V) silicate belong to the body centered cubic (bcc) system (43,44). The elementary cells of this material has an average lattice constant $a = 8.543\ A^{\circ}$.

The thermogravimetric analysis (Figure 4) shows the first inflection at $\sim 280^{\circ}C$ for the material corresponding to a 20% weight loss, which may be due to the removal of all the exchangeable water molecules from the gel. A further loss in weight above $280^{\circ}C$ may be due to the condensation process which is probably completed upto $400^{\circ}C$ beyond which the oxides of antimony and silicon are formed. An exhibition of the i.e.c. of the material even after heating to this temperature may be accounted for by the formation of antimonic acid when the oxide is dipped in aqueous solution.

On the basis of its chemical composition ph titration, IR spectra and TGA results, the antimony(V) silicate prepared in these studies, may be tentatively assigned the following formula:

$$\left[Sb_2O_5\ (H_2SiO_3)_6\right].nH_2O$$

If it is assumed that all the exchangeable water molecules are removed on heating upto $\sim 280^{\circ}C$, the first inflection in the TGA curve, the value of 'n' the external water molecules, can be calculated using Alberti's equation (45):

$$18\ n = \frac{X\,(M + 18n)}{100}$$

where, X is the % weight loss (20%) in the exchanger on heating

upto the inflection temperature.

M = molecular weight of the material minus the external water molecules.

The above equation then gives the external water molecules per molecule of antimony(V) silicate, as $\sim$ 11.

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CHAPTER - III

ION EXCHANGE KINETICS OF SOME DIVALENT METAL IONS ON ANTIMONY(V) SILICATE AND ANTIMONIC ACID CATION EXCHANGERS

Inorganic materials possessing ion exchange properties are well known for their metal ion selectivity (1). Since the kinetic studies of a reaction help in understanding the mechanism, it is worthwhile to conduct such a study on an ion exchanger. It will evaluate its separation potential. Earlier studies made in this direction (2-12) were based on the old Bt criterion (13) which should be useful only for an isotopic exchange process. In a true ion exchange phenomenon, however, different mobilities (14) of the exchanging ions are involved and hence for such a case Nernst-Planck equations (15,16) are more appropriate to obtain the precise values of the various kinetic parameters (17-19). Antimony(V) silicate has shown (20) a crystalline nature and promising ion exchange characteristics as described in Chapter II.

In view of this, the present chapter summarizes an effort to study the ion exchange kinetics on antimony(V) silicate and antimonic acid cation exchangers for the exchange of some divalent metal ions such as alkaline earths and transition metals.

EXPERIMENTAL

Reagents and chemicals

Antimony pentachloride ($SbCl_5$) used in this study was a product of Kochlight Laboratories Ltd. (Colonbrook Bucks, England) and sodium silicate ($Na_2SiO_3.3H_2O$) was a Riedal (DEHAENAG, Seelze Hannover) product. All other reagents and chemicals were either of BDH or AnalaR grade.

Apparatus

A water bath incubator shaker having a temperature variation of $\pm$ 0.5°C was used for the equilibrium studies.

Synthesis of the Ion Exchange Materials

Synthesis of antimony(V) silicate (SbSi)

The material was synthesized by the method as described in Chapter II.

Synthesis of antimonic acid (SbOH)

A 0.1M solution of antimony(V) chloride was hydrolyzed (21), and the precipitate was kept in the mother liquor for 6 days at room temperature ($\sim$30°C) before filtering, washing, drying, cracking and converting into the H^+ form as usual. Its Na^+ ion exchange capacity was found to be 1.9 meq/dry g.

Kinetic Measurements

The rates of exchange were determined by the limited bath technique (5) as follows:

The ion exchangers were ground and then sieved to obtain particles of different mesh sizes (25-50, 50-70, 70-100 and 100-150). The particles of mean radii $\sim$ 125 μm (50-70 mesh) were used for determining the various parameters. 20 ml fractions of the metal ion solutions of a constant ionic strength (2×10^{-2}N) were shaken with the exchanger beads (0.2 g) in a temperature controlled shaker at various temperatures (25°, 33°, 50° and 65°C) in several glass stoppered conical flasks for different time intervals. The supernatant liquid was removed immediately for its quantitative analysis.

The fractional attainment of equilibrium $U(\tau)$ was calculated by the equation:

$$U(\tau) = \frac{\text{the amount of exchange at time 't'}}{\text{the amount of exchange at infinite time}} \quad \ldots\ldots\ldots\ldots (1)$$

and the corresponding τ values were calculated by solving the Nernst-Planck equations (15,16). The τ values for alkaline earth and transition metal ions on SbSi and SbOH are given in Tables IX and X at four different temperatures.

TABLE - IX

τ VALUES FOR ALKALINE EARTH -H(I) EXCHANGES ON ANTIMONY(V) SILICATE AND ANTIMONIC ACID CATION EXCHANGERS AT DIFFERENT TEMPERATURES AFTER VARIOUS TIME INTERVALS

Mg(II) - H(I) Exchange

Time (min)	τ Values at			
	25°C	33°C	50°C	65°C
		Antimony(V) Silicate		
0.5	0.030	0.030	0.055	0.060
1.0	0.055	0.065	0.090	0.110
2.0	0.100	0.130	0.175	0.230
3.0	0.150	0.190	0.260	0.330
4.0	0.200	0.250	0.340	0.440
		Atimonic Acid		
0.5	0.030	0.040	0.055	0.060
1.0	0.060	0.080	0.095	0.120
1.5	0.090	0.120	0.150	0.170
2.0	0.125	0.140	0.180	0.230
2.5	0.145	0.180	0.230	0.300

TABLE - IX (Contd.)

Ca(II) - H(I) Exchange

Time (min)	τ Values at			
	25°C	33°C	50°C	65°C
		Antimony(V) Silicate		
0.5	0.010	0.015	0.018	0.015
1.0	0.020	0.030	0.030	0.040
2.0	0.045	0.055	0.060	0.080
3.0	0.065	0.075	0.095	0.095
4.0	0.085	0.100	0.120	0.150
		Antimonic Acid		
0.5	0.035	0.040	0.050	0.055
1.0	0.060	0.070	0.085	0.090
1.5	0.080	0.095	0.110	0.130
2.0	0.105	0.120	0.140	0.170
2.5	0.130	0.155	0.170	0.210

TABLE - IX (Contd.)

Sr(II) - H(I) Exchange

Time (min)	T Values at 25°C	33°C	50°C	65°C
		Antimony(V) Silicate		
0.5	0.010	0.020	0.020	0.025
1.0	0.025	0.035	0.040	0.050
2.0	0.040	0.060	0.065	0.085
3.0	0.065	0.080	0.085	0.095
4.0	0.080	0.115	0.120	0.140
		Antimonic Acid		
0.5	0.025	0.030	0.035	0.040
1.0	0.045	0.050	0.060	0.075
1.5	0.060	0.070	0.080	0.105
2.0	0.085	0.095	0.105	0.140
2.5	0.100	0.110	0.130	0.170

TABLE - IX (Contd.)

Ba(II) - H(I) Exchange

Time (min)	τ Values at			
	25°C	33°C	50°C	65°C
	Antimony(V) Silicate			
0.5	0.020	0.020	0.030	0.018
1.0	0.040	0.050	0.060	0.060
2.0	0.070	0.075	0.090	0.105
3.0	0.095	0.110	0.150	0.170
4.0	0.120	0.135	0.200	0.225
	Antimonic Acid			
0.5	0.030	0.035	0.040	0.050
1.0	0.050	0.060	0.080	0.100
1.5	0.075	0.090	0.100	0.120
2.0	0.095	0.120	0.140	0.160
2.5	0.125	0.140	0.160	0.190

TABLE - X

$\mathcal{T}$ VALUES FOR TRANSITION METAL -H(I) EXCHANGES ON ANTIMONY(V) SILICATE AND ANTIMONIC ACID CATION EXCHANGERS AT DIFFERENT TEMPERATURES AFTER VARIOUS TIME INTERVALS

Mn(II) - H(I) Exchange

Time (min)	$\mathcal{T}$ Values at 25°C	33°C	50°C	65°C
	Antimony(V) Silicate			
0.5	0.020	0.025	0.040	0.050
1.0	0.035	0.045	0.060	0.085
2.0	0.065	0.095	0.120	0.145
3.0	0.090	0.145	0.150	0.200
4.0	0.013	0.190	0.235	0.285
	Antimonic Acid			
0.5	0.015	0.020	0.025	0.030
1.0	0.030	0.035	0.045	0.060
1.5	0.055	0.075	0.100	0.095
2.0	0.090	0.095	0.135	0.145
2.5	0.115	0.140	0.180	0.185

TABLE - X (Contd.)

Fe(II) - H(I) Exchange

Time (min)	T Values at 25°C	33°C	50°C	65°C
		Antimony(V) Silicate		
0.5	0.015	0.020	0.025	0.030
1.0	0.030	0.035	0.045	0.060
2.0	0.055	0.075	0.100	0.095
3.0	0.090	0.095	0.135	0.145
4.0	0.115	0.140	0.180	0.185
		Antimonic Acid		
0.5	0.025	0.035	0.040	0.050
1.0	0.048	0.060	0.070	0.090
1.5	0.070	0.090	0.110	0.125
2.0	0.090	0.110	0.140	0.175
2.5	0.115	0.140	0.175	0.210

TABLE - X (Contd.)

Co(II) - H(I) Exchange

Time (min)	τ Values at 25°C	33°C	50°C	65°C
		Antimony(V) Silicate		
0.5	0.015	0.025	0.030	0.045
1.0	0.025	0.045	0.075	0.085
2.0	0.050	0.075	0.115	0.150
3.0	0.075	0.125	0.210	0.230
4.0	0.012	0.165	0.250	0.315
		Antimonic Acid		
0.5	0.035	0.035	0.050	0.050
1.0	0.060	0.065	0.080	0.100
1.5	0.080	0.100	0.110	0.150
2.0	0.110	0.130	0.160	0.200
2.5	0.130	0.150	0.195	0.240

TABLE - X (Contd.)

Ni(II) - H(I) Exchange

Time (min)	τ Values at			
	25°C	33°C	50°C	65°C
	Antimony(V) Silicate			
0.5	0.015	0.020	0.025	0.030
1.0	0.030	0.040	0.045	0.055
2.0	0.050	0.070	0.080	0.095
3.0	0.070	0.100	0.130	0.140
4.0	0.095	0.130	0.170	0.195
	Antimonic Acid			
0.5	0.030	0.035	0.040	0.055
1.0	0.055	0.065	0.080	0.095
1.5	0.075	0.090	0.115	0.140
2.0	0.090	0.120	0.150	0.180
2.5	0.115	0.150	0.195	0.240

DISCUSSION

A study of the concentration effect on the rate of exchange at 33°C shows that the initial rate of exchange is proportional to the metal ion concentration in the range less than 2×10^{-2} N, while it is independent at and above this concentration suggesting a particle diffusion phenomenon. In this respect both these ion exchangers (SbSi and SbOH) are similar to the materials of this class (17-19).

Although this is a limited bath system, the equation applicable to an infinite bath can be used here because $CV >> \bar{C}\bar{V}$ where C and $\bar{C}$ are the metal ion concentrations in the solution and exchanger phases respectively, V and $\bar{V}$ are the volumes of these two phases. The Nernst-Planck equations can be solved with some additional assumptions (22), which are valid for inorganic ion exchangers as the swelling changes and the specific interactions are not significant in this case. As a result, we obtain a coupled interdiffusion coefficient $\bar{D}_{AB}$, the value of which depends on the relative concentrations of the counter ions A and B in the exchanger phase ($\bar{C}_A$ and $\bar{C}_B$). For $\bar{C}_A << \bar{C}_B$ the interdiffusion coefficient assumes the value $\bar{D}_A$. The counter ion A being initially present in the ion exchanger phase. In the present study since the exchanger is taken in H^+ form, $\bar{D}_A$ may be replaced by $\bar{D}_H$.

Thus on the basis of the Nernst-Planck equations the numerical results are expressed by the explicit approximation (23),

$$U(\tau) = \left\{1 - \exp\left[\pi^2\left(f_1(\alpha)\tau + f_2(\alpha)\tau^2 + f_3(\alpha)\tau^3\right)\right]\right\}^{\frac{1}{2}} \quad \ldots.(2)$$

where $\tau = \dfrac{\bar{D}_H t}{ro^2}$

and the mobility ratio $\alpha = \dfrac{\bar{D}_H}{\bar{D}_M}$, ro = particle radius and $\bar{D}_M$ is the interdiffusion coefficient of the metal ion. Under the conditions $1 \leqslant \alpha \leqslant 20$ and the charge ratio $Z_H / Z_m = \frac{1}{2}$ as in the present case, the three functions $f_1(\alpha)$, $f_2(\alpha)$ and $f_3(\alpha)$ can be expressed as:

$$f_1(\alpha) = -\frac{1}{0.64 + 0.36\alpha^{0.668}} \quad \ldots\ldots\ldots \quad (a)$$

$$f_2(\alpha) = -\frac{1}{0.96 - 2.0\,\alpha^{0.4635}} \quad \ldots\ldots\ldots \quad (b)$$

and $$f_3(\alpha) = -\frac{1}{0.27 + 0.09\,\alpha^{1.14}} \quad \ldots\ldots\ldots \quad (c)$$

Each value of $U(\tau)$ will have a corresponding value of τ which is obtained on solving equation no. 2.

The plots of τ versus time at the four different temperatures (Figures 12 to 15) for alkaline earth and transition metal ions on SbSi and SbOH are shown at a concentration 0.02N which are straight lines passing through the origin. It confirms a particle diffusion controlled phenomenon. The results are summarized in Tables IX and X for all the M(II) - H(I) exchanges on these materials.

The particle size of the exchanger has a marked effect on the rate of exchange. A plot of τ versus time for four particle sizes of the exchangers shows that the rate of exchange is inversely proportional to the square of the particle radius, which is in agreement with the fundamental condition of the particle diffusion (Figures 16 and 17). Tables XI and XII summarize the results for Mg(II)-H(I) and Mn(II)-H(I) exchanges on both these exchangers.

The slopes (S) of various τ versus time plots for all the metal ions on SbSi and SbOH are given in Tables XIII and XIV. They are related with $\bar{D}_H$ as follows:

$$S = \frac{\bar{D}_H}{ro^2} \qquad \ldots\ldots\ldots \quad (3)$$

The S values are different for the different particle radii of the exchangers as observed for Mg(II) and Mn(II) ions at

33°C, plotted against $\frac{1}{r^2}$ as shown in Figures 18 and 19. These figures show that the rate of exchange in antimonic acid is faster than antimony(V) silicate.

The plots of -log $\overline{D}_H$ versus 1/T are straight lines as shown in Figures 20 and 21, verifying the Arrhenius relation:

$$\overline{D}_H = D_o \exp^{(-E_a/RT)} \quad \ldots\ldots\ldots \quad (4)$$

D_o is obtained by extrapolating these lines and observing the intercepts at the origin. The activation energy (E_a) is then calculated with the help of the equation no. 4 putting the value of $\overline{D}_H$ at 273°K. Finally, the entropy of activation ($\triangle S^*$) is calculated by the equation:

$$D_o = 2.72\, d^2 \frac{kT}{h} \exp\left(\triangle S^*/R\right) \quad \ldots\ldots\ldots\ldots\ldots \quad (6)$$

where d is the ionic jump distance (24) taken as 5A°, k is the Boltzmann constant and h is the planck's constant. T is taken as 273°k. The values of D_o, E_a and $\triangle S^*$ for SbSi and SbOH are summarized in Tables XV and XVI. The results show that there is no definite relation between ionic radii of the metal ions and the values of E_a and $\triangle S^*$. Negative $\triangle S^*$ values indicate that the behaviour of SbSi and SbOH is similar to that of Zr(IV) and Th(IV) phosphosilicate (18) for transition metal ions. The value

of ΔS^* is maximum for Ca(II) ion on antimony(V) silicate while it is maximum for Ba(II) ion on antimonic acid. In case of the transition metal ions the value of ΔS^* is maximum for Fe(II) in both these exchangers. E_a values for Ca(II), Sr(II) and Ba(II) are similar, to some extent on both the exchangers. However, it is appreciably greater for the Mg(II) ion. In case of the transition metals, the values are widely different on SbSi while they are almost similar on SbOH.

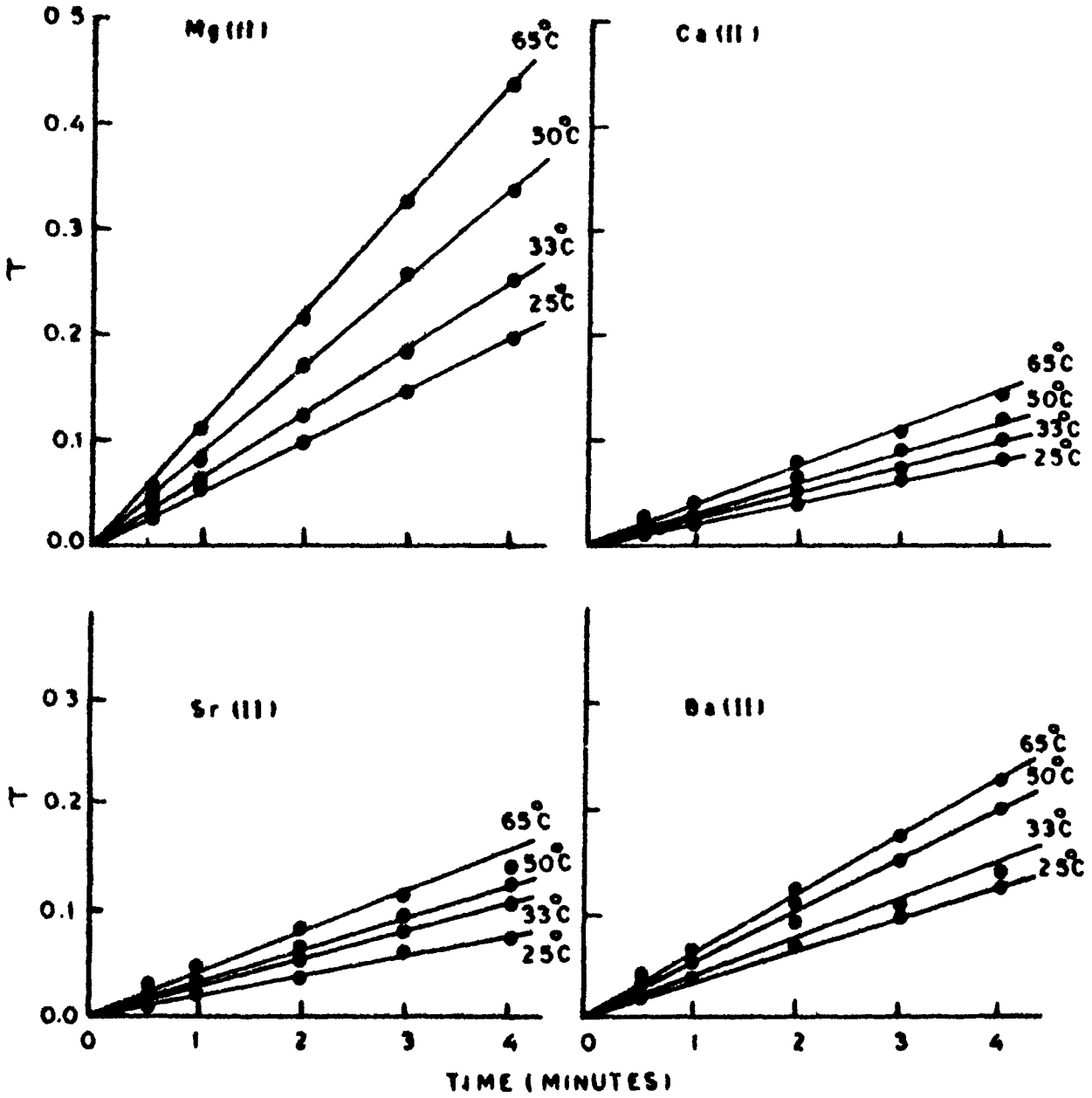

FIG. 12 T VERSUS TIME PLOTS FOR ALKALINE EARTH-H(I) EXCHANGES ON ANTIMONY (V) SILICATE AT FOUR DIFFERENT TEMPERATURES

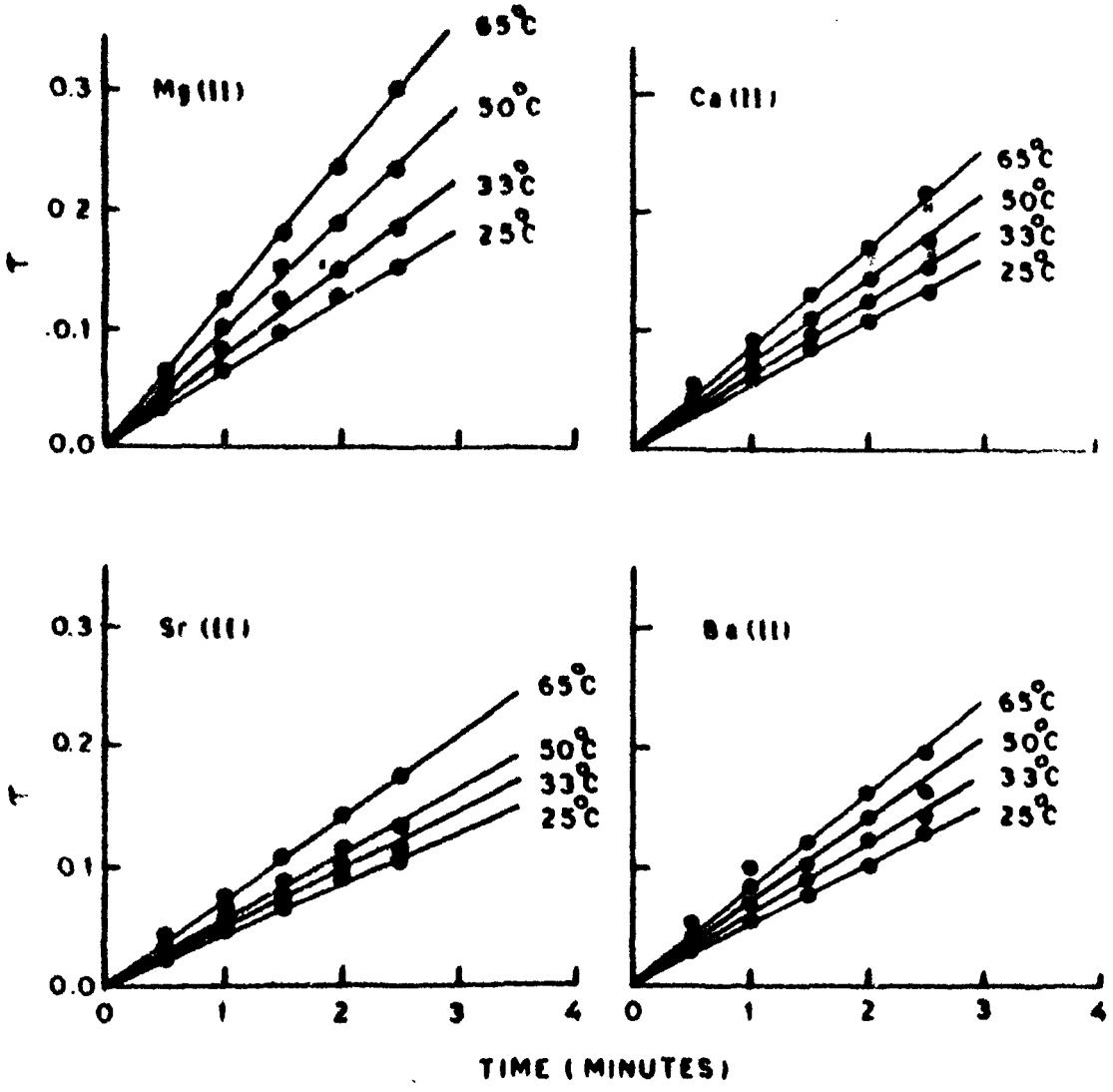

FIG. 13 τ VERSUS TIME PLOTS FOR ALKALINE EARTH – H(I) EXCHANGES ON ANTIMONIC ACID AT FOUR DIFFERENT TEMPERATURES

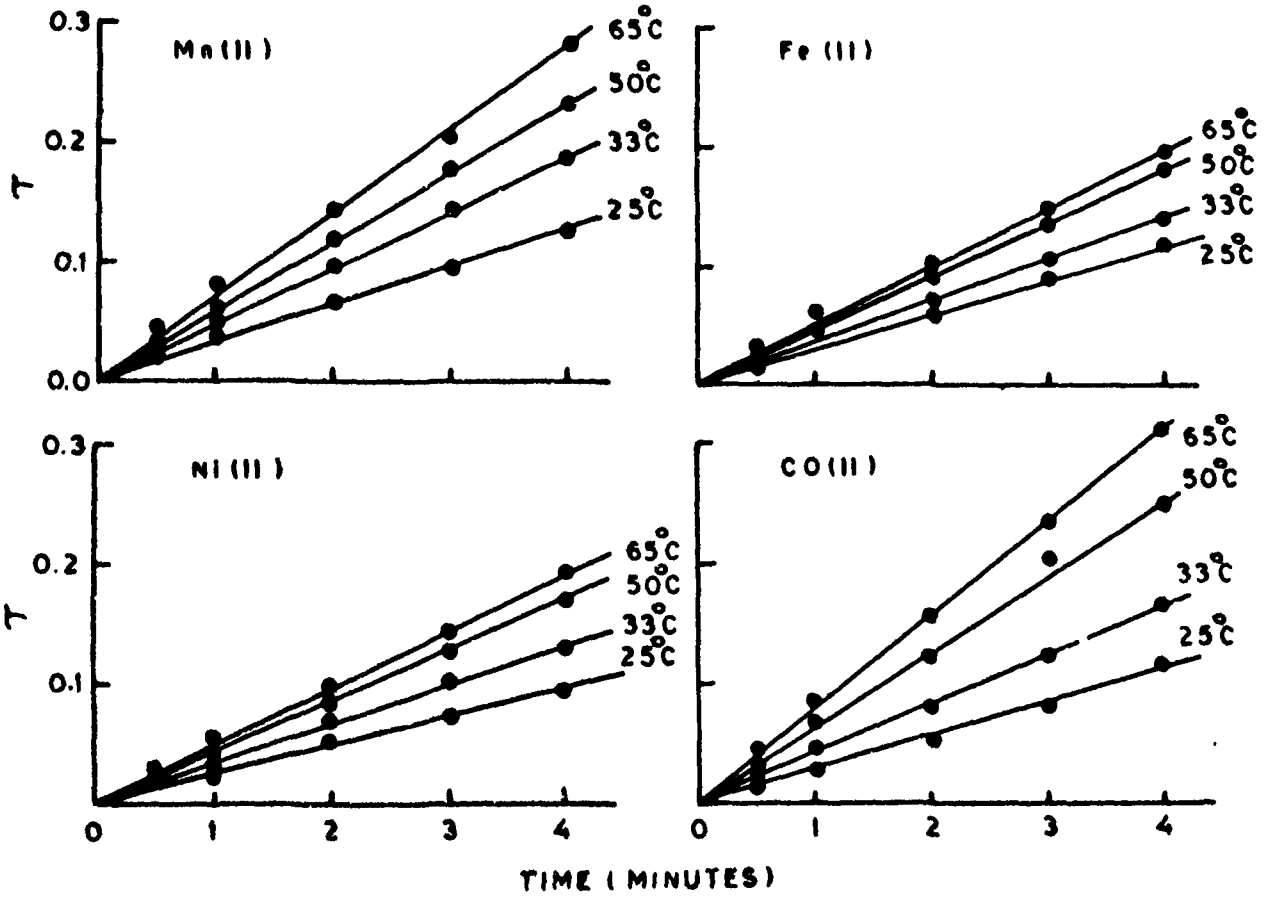

FIG. 14 T VERSUS TIME PLOTS FOR TRANSITION METAL – H(I)EXCHANGES ON ANTIMONY (V)SILICATE AT FOUR DIFFERENT TEMPERATURES

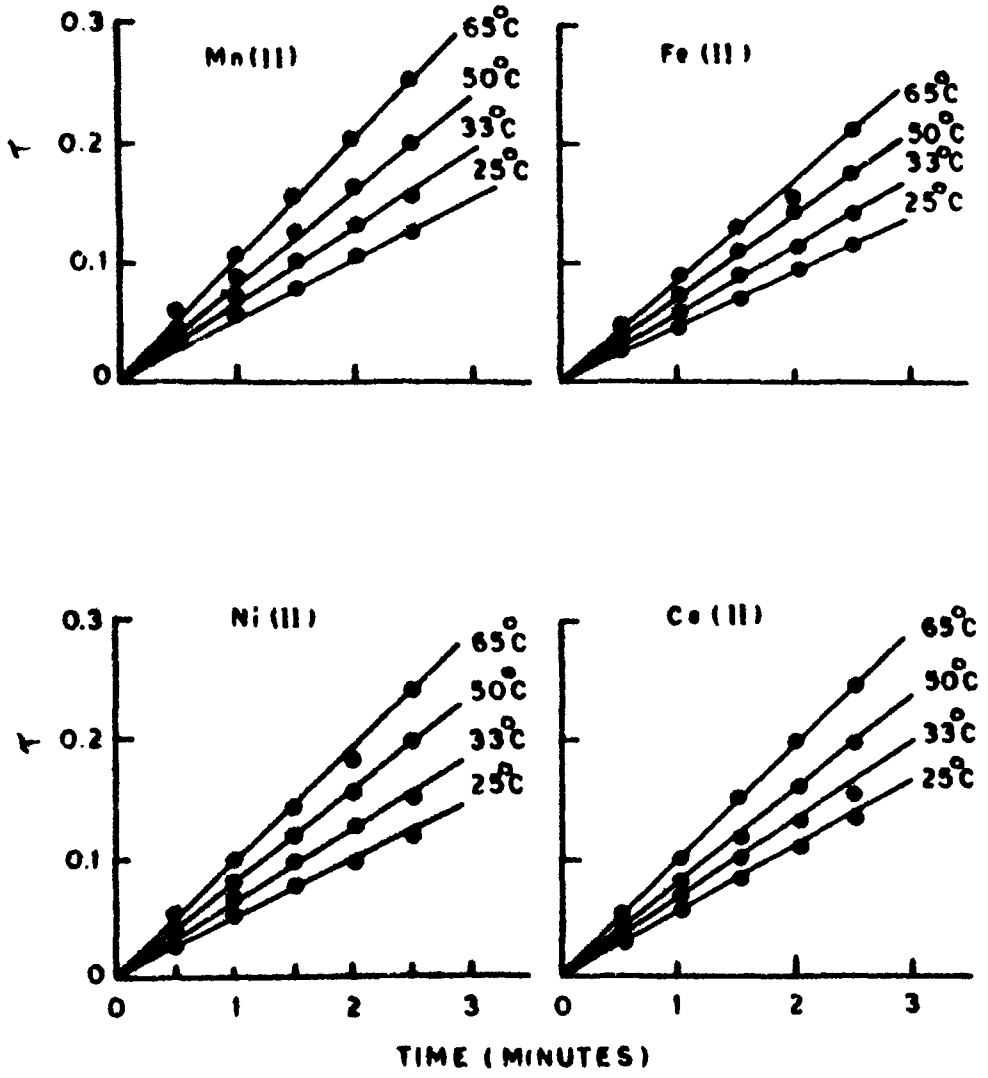

FIG. 15 T VERSUS TIME PLOTS FOR TRANSITION METAL-H (I) EXCHAGES ON ANTIMONIC ACID AT FOUR DIFFERENT TEMPERATURES

TABLE - XI

τ VALUES FOR THE Mg(II) - H(I) EXCHANGE AT 33 ± 0.5°C ON ANTIMONY(V) SILICATE AND ANTIMONIC ACID CATION EXCHANGERS OF VARIOUS PARTICLE SIZES

Mg(II) - H(I) Exchange

Time (min)	τ Values for the particle sizes			
	225 µm	125 µm	78.6 µm	62.5 µm
		Antimony(V) Silicate		
0.5	0.030	0.030	0.045	0.050
1.0	0.055	0.065	0.080	0.090
2.0	0.105	0.130	0.155	0.170
3.0	0.160	0.190	0.225	0.275
4.0	0.210	0.250	0.320	0.350
		Antimonic Acid		
0.5	0.015	0.040	0.045	0.050
1.0	0.055	0.065	0.075	0.095
1.5	0.080	0.100	0.110	0.130
2.0	0.100	0.130	0.140	0.175
2.5	0.120	0.150	0.170	0.200

TABLE - XII

τ VALUES FOR THE Mn(II) - H(I) EXCHANGE AT 33 ± 0.5°C ON ANTIMONY(V) SILICATE AND ANTIMONIC ACID CATION EXCHANGERS OF VARIOUS PARTICLE SIZES

Mn(II) - H(I) Exchange

Time (min)	τ Values for the particle sizes			
	225 μm	125 μm	78.6 μm	62.5 μm
	Antimony(V) Silicate			
0.5	0.025	0.025	0.035	0.045
1.0	0.040	0.045	0.060	0.070
2.0	0.080	0.095	0.110	0.120
3.0	0.115	0.145	0.165	0.185
4.0	0.150	0.190	0.215	0.250
	Antimonic Acid			
0.5	0.030	0.040	0.045	0.050
1.0	0.055	0.080	0.085	0.100
1.5	0.080	0.120	0.125	0.145
2.0	0.120	0.140	0.170	0.200
2.5	0.145	0.180	0.215	0.245

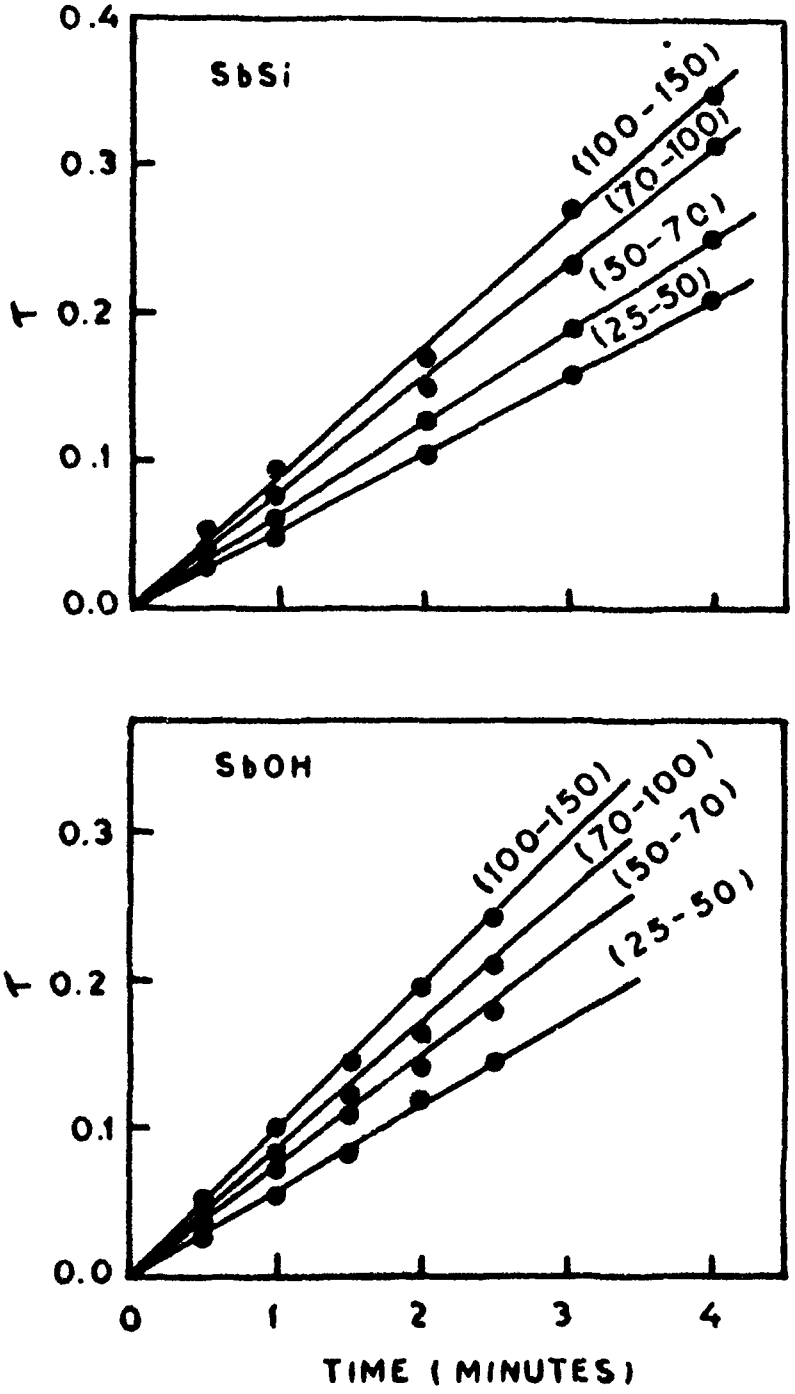

FIG. 16 INFLUENCE OF THE PARTICLE SIZE ON THE EXCHANGE RATE OF THE Mg(II)-H(I) EXCHANGE ON ANTIMONY(V) SILICATE AND ANTIMONIC ACID

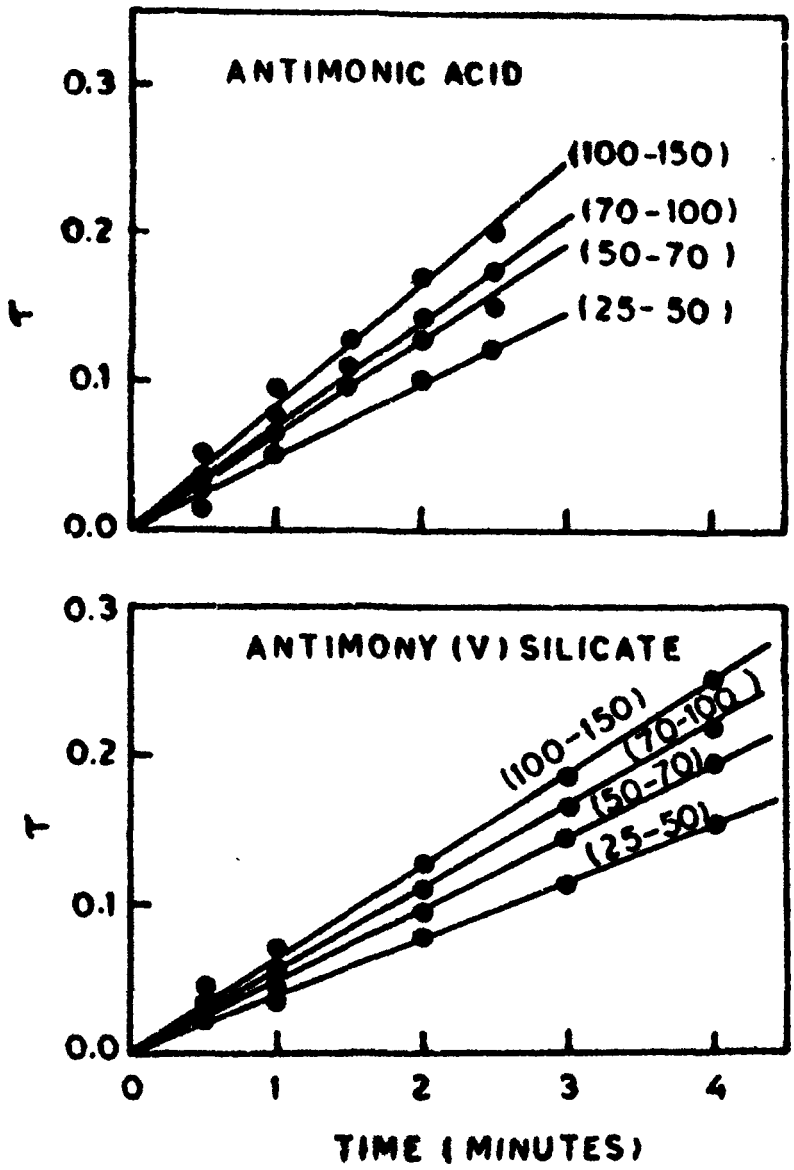

FIG. 17 INFLUENCE OF THE PARTICLE SIZE ON THE EXCHANGE RATE OF THE Mn(II)- H(I) EXCHANGE ON ANTIMONY(V) SILICATE AND ANTIMONIC ACID

TABLE - XIII

SLOPES (S) OF THE VARIOUS T' VERSUS TIME PLOTS AT DIFFERENT TEMPERATURES FOR ALKALINE EARTH -H(I) EXCHANGES ON ANTIMONY(V) SILICATE AND ANTIMONIC ACID CATION EXCHANGERS OF VARIOUS PARTICLE SIZES

Metal Ion	Particle radius (μm)	S x 10^{-4} (Sec^{-1}) values at							
		Antimony(V) Silicate				Antimonic Acid			
		25°C	33°C	50°C	65°C	25°C	33°C	50°C	65°C
Mg(II)	225	-	8.75	-	-	-	9.44	-	-
Mg(II)	125	8.33	10.42	14.17	18.33	10.00	12.78	15.83	20.00
Mg(II)	78.6	-	12.92	-	-	-	14.17	-	-
Mg(II)	62.5	-	14.58	-	-	-	16.67	-	-
Ca(II)	125	3.60	4.20	5.00	6.25	8.89	10.56	12.22	14.17
Sr(II)	125	5.33	5.00	5.40	6.80	7.08	7.92	9.17	11.67
Ba(II)	125	5.20	6.25	8.17	9.40	8.33	10.00	11.67	13.33

TABLE - XIV

SLOPES OF THE VARIOUS $\bar{F}$ VERSUS TIME PLOTS AT DIFFERENT TEMPERATURES FOR TRANSITION METAL -H(I) EXCHANGES ON ANTIMONY(V) SILICATE AND ANTIMONIC ACID CATION EXCHANGERS OF VARIOUS PARTICLE SIZES

Metal Ion	Particle radius (μm)	S x 10^{-4} (Sec^{-1}) Values at							
		Antimony(V) Silicate				Antimonic Acid			
		25°C	33°C	50°C	65°C	25°C	33°C	50°C	65°C
Mn(II)	225	-	6.25	-	-	-	8.33	-	-
Mn(II)	125	5.42	7.92	9.79	11.88	8.33	10.83	13.33	16.67
Mn(II)	78.6	-	9.17	-	-	-	12.22	-	-
Mn(II)	62.5	-	10.42	-	-	-	13.89	-	-
Fe(II)	125	4.79	5.83	7.50	8.13	7.50	9.58	11.67	14.17
Co(II)	125	4.79	6.88	10.42	13.13	9.17	10.83	13.33	16.67
Ni(II)	125	4.17	5.63	7.08	7.92	8.33	10.42	13.33	16.25

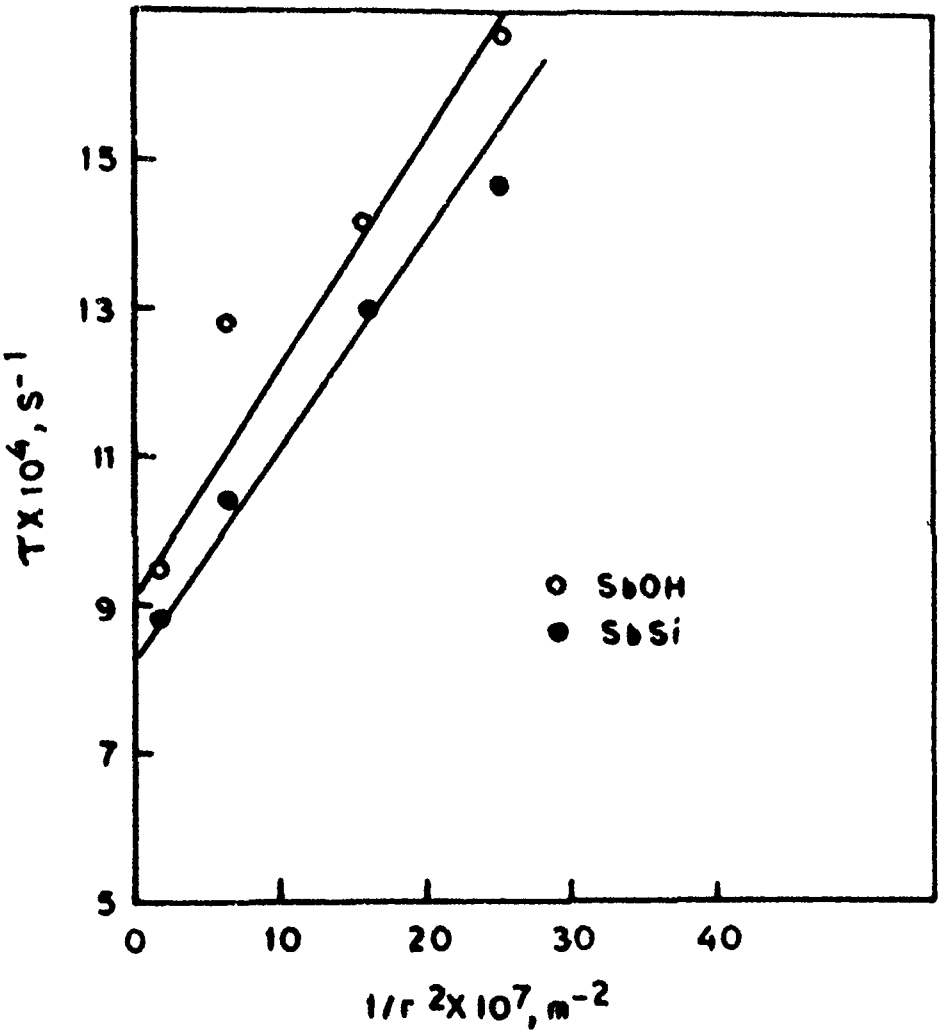

FIG. 18 SLOPES (S) VERSUS $1/r^2$ PLOTS FOR THE Mg (II) – H(I) EXCHANGE ON ANTIMONY (V) SILICATE AND ANTIMONIC ACID

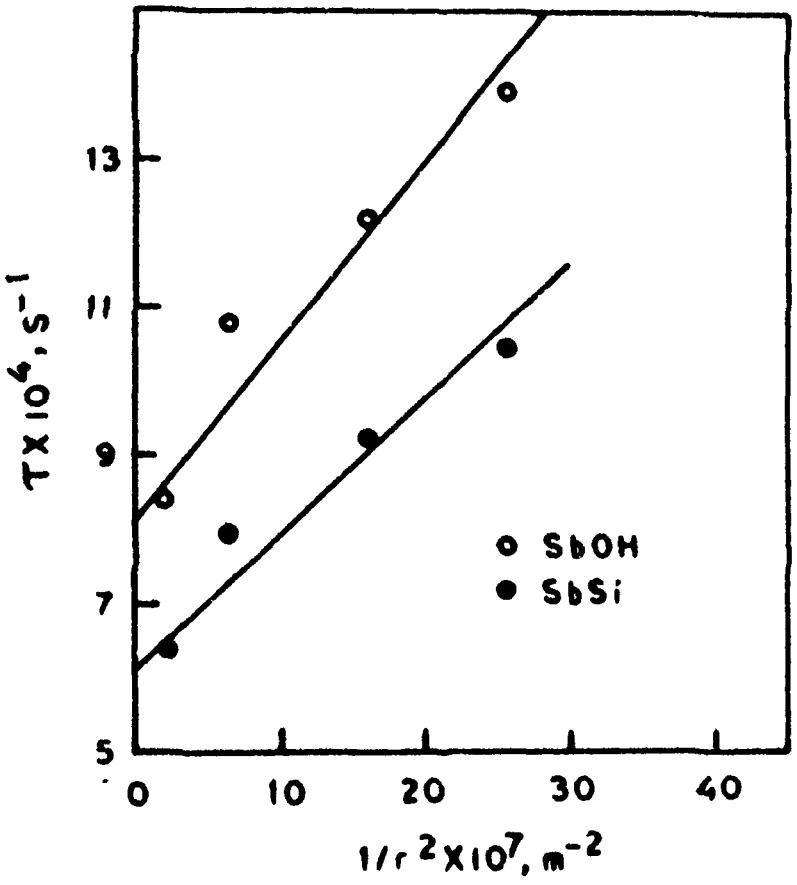

FIG. 19 SLOPES (S) VERSUS $1/r^2$ PLOTS FOR THE Mn (II) - H (I) EXCHANGE ON ANTIMONY (V) SILICATE AND ANTIMONIC ACID

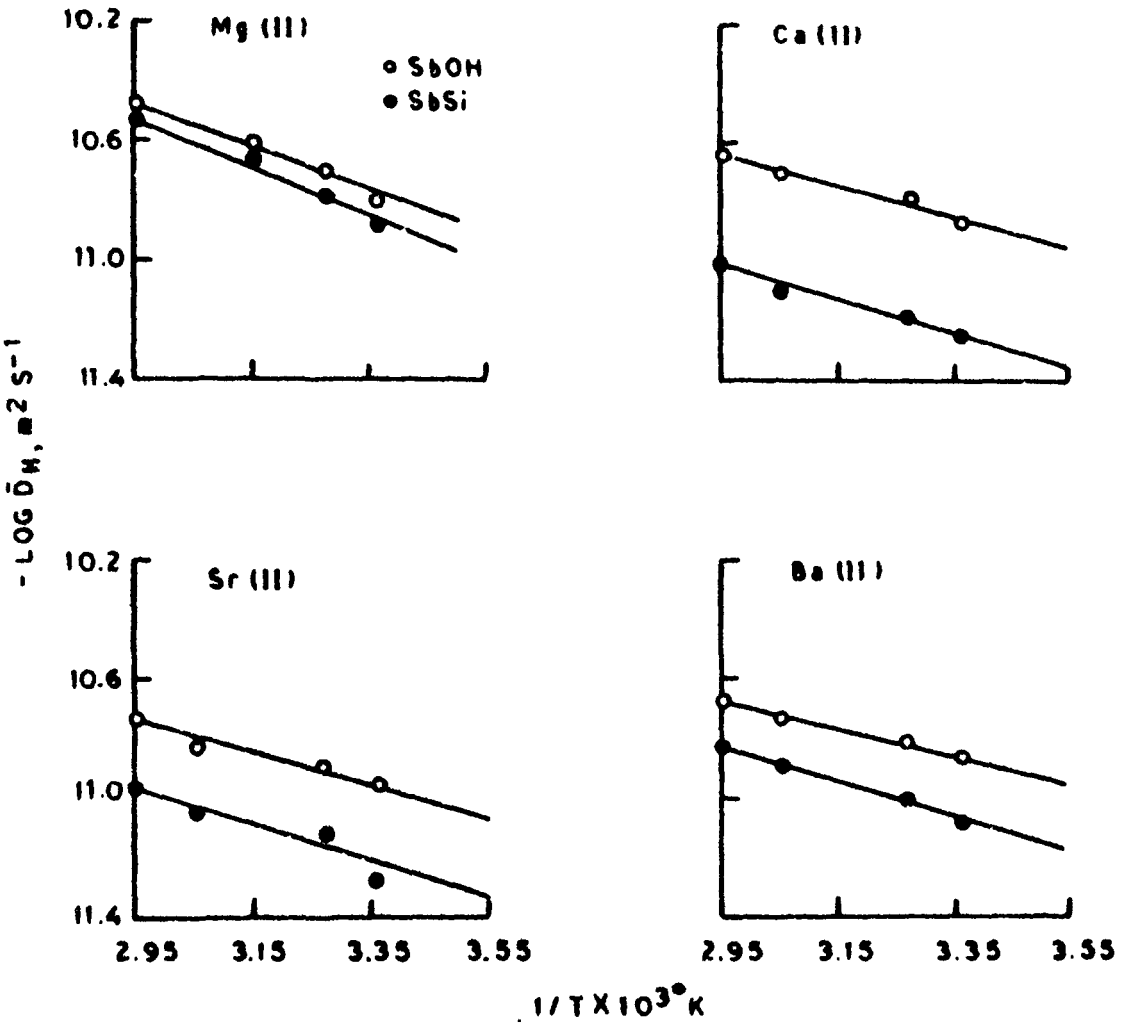

FIG. 20 -LOG $\bar{D}H$ VERSUS 1/T PLOTS FOR THE ALKALINE EARTH-H(I) EXCHANGES ON ANTIMONY(V) SILICATE AND ANTIMONIC ACID

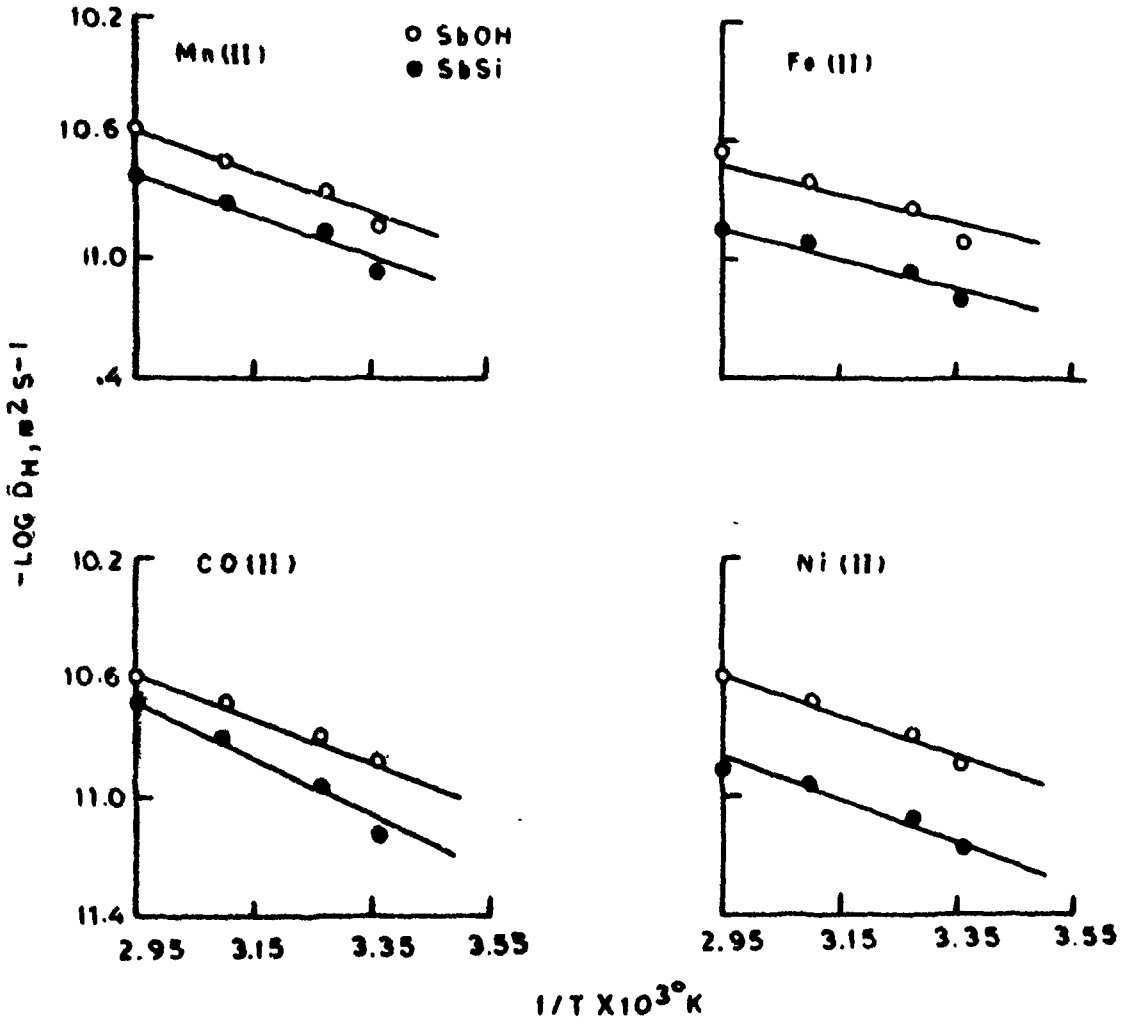

FIG.21 -LOG $\bar{D}_H$ VERSUS 1/T PLOTS FORTHE TRANSITION METAL-H(I) EXCHANGES ON ANTIMONY(V)SILICATE AND ANTIMONIC ACID

TABLE - XV

SELF DIFFUSION COEFFICIENT, ENERGY OF ACTIVATION AND ENTROPY OF ACTIVATION OF ALKALINE EARTH -H(I) EXCHANGES ON ANTIMONY(V) SILICATE AND ANTIMONIC ACID CATION EXCHANGERS

Migrating Ion	Ionic Mobility ($m^2 Volt^{-1} Sec^{-1}$)	Ionic Radii (nm)	D_o, E_a and ΔS^* Values					
			Antimony(V) Silicate			Antimonic Acid		
			D_o ($m^2 Sec^{-1}$)	E_a ($KJ\ mole^{-1}$)	ΔS^* ($JK^{-1} mole^{-1}$)	D_o ($m^2 Sec^{-1}$)	E_a ($KJ\ mole^{-1}$)	ΔS^* ($JK^{-1} mole^{-1}$)
Mg(II)	55×10^{-9}	7.8×10^{-2}	7.59×10^{-9}	15.63	-51.83	3.16×10^{-9}	12.93	-59.11
Ca(II)	62×10^{-9}	10.6×10^{-2}	5.13×10^{-10}	11.13	-74.23	7.24×10^{-10}	9.72	-71.36
Sr(II)	62×10^{-9}	12.7×10^{-2}	5.50×10^{-10}	11.19	-73.65	9.33×10^{-10}	10.98	-69.25
Ba(II)	66×10^{-9}	14.3×10^{-2}	8.32×10^{-10}	11.24	-70.21	5.50×10^{-10}	9.17	-73.65

Average radius of the exchanger particles used = 125 μm

TABLE - XVI

SELF DIFFUSION COEFFICIENT, ENERGY OF ACTIVATION AND ENTROPY OF ACTIVATION OF TRANSITION METAL -H(I) EXCHANGES ON ANTIMONY(V) SILICATE AND ANTIMONIC ACID CATION EXCHANGERS

Migrating Ion	Ionic Mobility ($m^2 Volt^{-1} Sec^{-1}$)	Ionic Radii (nm)	D_o, E_a and ΔS^* Values					
			Antimony(V) Slicate			Antimonic Acid		
			D_o ($m^2 Sec^{-1}$)	E_a ($KJ\ mole^{-1}$)	ΔS^* ($JK^{-1} mole^{-1}$)	D_o ($m^2 Sec^{-1}$)	E_a ($KJ\ mole^{-1}$)	ΔS^* ($JK^{-1} mole^{-1}$)
Mn(II)	55×10^{-9}	9.1×10^{-2}	1.45×10^{-9}	12.34	-65.59	2.19×10^{-9}	12.55	-62.16
Fe(II)	54×10^{-9}	8.3×10^{-2}	2.88×10^{-10}	8.94	-79.03	4.57×10^{-10}	11.15	-75.19
Co(II)	55×10^{-9}	8.2×10^{-2}	8.71×10^{-9}	17.19	-50.68	3.98×10^{-9}	14.48	-57.19
Ni(II)	52×10^{-9}	7.8×10^{-2}	1.58×10^{-9}	13.48	-64.87	1.95×10^{-9}	12.33	-63.12

Average radius of the exchanger particles used = 125 μm

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CHAPTER - IV

THERMODYNAMICS OF Mg(II), Ca(II), Sr(II) AND Ba(II) EXCHANGES ON ANTIMONY(V) SILICATE CATION EXCHANGER

Inorganic ion exchangers have received sufficient attention as a separating medium for metal ions. Although a large number of such materials have been synthesized earlier (1), only a few of them have been studied thoroughly for their ion exchange behaviour on the basis of a fundamental approach such as thermodynamics. This approach is more appropriate for describing equilibria of a system consisting of an ion exchanger and an aqueous solution containing the exchangeable ions. Such studies have been performed on the crystalline and amorphous zirconium phosphate (2-9), crystalline titanium phosphate (10), amorphous cerium phosphate (11), antimony phosphate (12), titanium and vanadium oxide (13), tindioxide (14), manganese and nickel tungstate (15), zirconium arsenate (16), tantalum arsenate (17), iron antimonate (18) and crystalline antimonic acid (19). The present chapter summarizes a detailed and systematic thermodynamic study for the Mg(II) - H(I), Ca(II) - H(I), Sr(II) - H(I) and Ba(II) - H(I) exchanges on antimony(V) silicate cation exchanger in order to have an understanding of the exchange process occurring on this material.

EXPERIMENTAL

Reagents and chemicals

Antimony(V) chloride ($SbCl_5$) used in this study was a product of Kochlight Laboratories Ltd. (Colnbrook Bucks, England) and sodium silicate ($Na_2SiO_3.3H_2O$) was a riedal (DEHAENAG, Seelze Hannover) product. Other reagents and chemicals were either of BDH or AnalaR grade.

Apparatus

A water bath incubator shaker having a temperature variation of $\pm$ 0.5°C was used for the equilibrium studies.

Synthesis of antimony(V) silicate (SbSi)

The ion exchange material was synthesized by the process as described in Chapter II.

Equilibrium experiments

Two hundred milligrams of the exchanger in H^+ form were shaken for 3 hours in various stoppered conical flasks at a desired temperature (25°C or 50°C), with 20 ml solution of the metal ion having a constant ionic strength (0.03M) adjusted by adding the appropriate amounts of HNO_3. The shaking time of 3 hours was selected because the equilibrium was attained within this period as

indicated in Figures 22 and 23. The supernatant solution was analysed for the metal and hydrogen ions by the ordinary chemical methods.

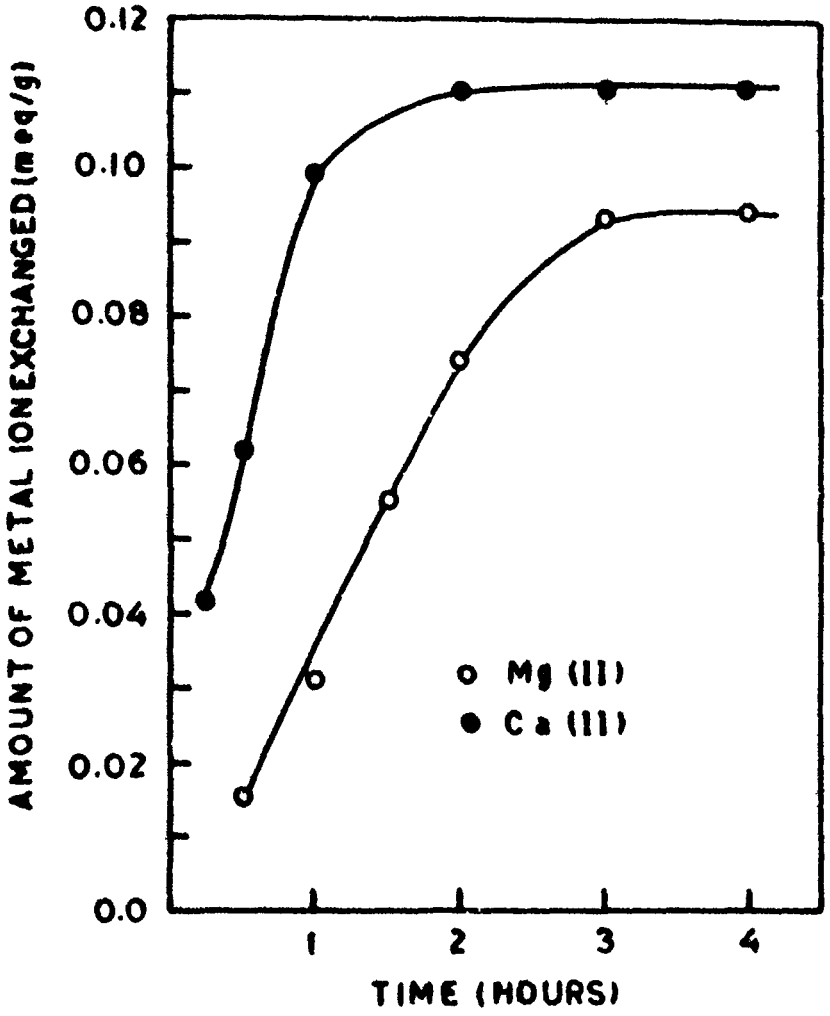

FIG. 22 PLOTS OF THE AMOUNT EXCHANGED OF Mg (II) AND Ca (II) WITH H(I) VERSUS TIME ON ANTIMONY(V) SILICATE CATION EXCHANGER

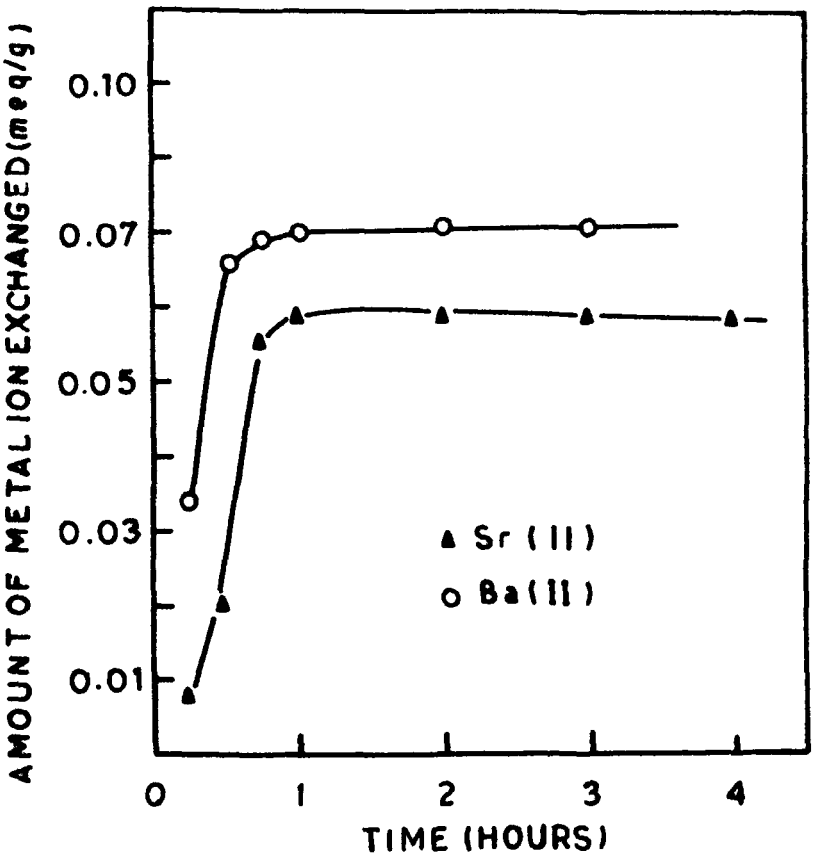

FIG. 23 PLOTS OF THE AMOUNT EXCHANGED OF Sr (II) AND Ba(II) WITH H(I) VERSUS TIME ON ANTIMONY(V) SILICATE CATION EXCHANGER

DISCUSSION

The exchange reaction between SbSi in H^+ form and the metal ions in solution can be represented by the equation:

$$2H\,SbSi + M(II) \rightleftharpoons M(SbSi)_2 + 2H(I) \qquad - - - - - - - (1)$$

where M(II) represents the metal ions (Mg(II), Ca(II), Sr(II) and Ba(II) ions).

It is clear from Figure 22 that the equilibrium has been attained within 3 hours for the Mg(II) - H(I) exchange. However, for the Ca(II)- H(I), Sr(II)- H(I), and Ba(II) - H(I) exchanges (Figure 23) the result is obtained only after one hour shaking. The interactions may be described as follows:

$$\overline{C}_H + C_M \rightleftharpoons \overline{C}_M + C_H \qquad - - - - - - - (2)$$

where the barred and unbarred quantities represents the equivalent concentrations in the exchanger and solution phases respectively.

The equivalent ionic fractions of the counter ions in the exchanger and solution phases $\overline{X}_M$, $\overline{X}_H$, X_M and X_H were calculated by the expressions:

$$\overline{X}_M = \frac{\overline{C}_M}{\overline{C}}, \quad X_M = \frac{C_M}{C}, \quad \overline{X}_H = \frac{\overline{C}_H}{\overline{C}} \text{ and } X_H = \frac{C_H}{C}$$

where $\overline{C}$ and C are the total electrolyte concentrations in the solid and solution phases respectively.

To examine the affinity for the interacting ions, the separation factors were calculated by the following equation:

$$\alpha_{H}^{M} = \frac{\overline{X}_M}{\overline{X}_H} \cdot \frac{X_H}{X_M} \qquad \text{- - - - - - - (3)}$$

The selectivity coefficients were calculated (20) by the following expression, assuming the ratio of activity coefficients in the solution to be unity (21). Under these conditions K_c ceases to express interactions in solution.

$$K_c = \frac{\overline{m}_M}{(\overline{m}_H)^2} \cdot \frac{(m_H)^2}{m_M} \qquad \text{- - - - - - - - (4)}$$

where m_M and $\overline{m}_M$ are the molalities of the metal ions in the solution and exchanger phases respectively, m_H and $\overline{m}_H$ are the molalities of H(I) ions in these two phases. The values obtained at 25° and 50°C are summarized in Tables XVII to XX, while Figures 24 and 25 show the exchange isotherms. It is clear from Figure 24 that in the Mg(II) - H(I) exchange the material has a preference for H(I) ions at both the temperatures over the entire range of concentrations studied. However, in case of the Ca(II)- H(I) and Sr(II) - H(I) exchanges the reverse is true i.e. Ca(II) and Sr(II) ions are adsorbed preferably by the SbSi phase at all the concentrations, and the preference being higher at a higher temperature i.e. at 50°C.

TABLE - XVII

EQUIVALENT IONIC FRACTIONS, SEPARATION FACTORS, MOLALITIES AND SELECTIVITY COEFFICIENTS FOR THE Mg(II)- H(I) EXCHANGE ON ANTIMONY(V) SILICATE CATION EXCHANGER

Sl. No.	$\overline{X}_{Mg}$	$\overline{m}_{Mg}$	X_{Mg}	m_{Mg}	$\overline{X}_H=\overline{m}_H$	$X_H=m_H$	α_H^{Mg}	K_c	log K_c
				At 25°C					
1.	0.10	0.05	0.20	0.10	0.88	0.43	0.25	0.12	-0.92
2.	0.12	0.06	0.25	0.13	0.84	0.31	0.18	0.07	-1.18
3.	0.13	0.07	0.32	0.16	0.83	0.27	0.13	0.04	-1.38
4.	0.17	0.08	0.45	0.23	0.80	0.24	0.11	0.03	-1.48
5.	0.19	0.09	0.46	0.23	0.78	0.22	0.12	0.03	-1.51
6.	0.20	0.10	0.57	0.29	0.76	0.19	0.09	0.02	-1.68
7.	0.22	0.11	0.65	0.31	0.76	0.17	0.08	0.02	-1.72
8.	0.27	0.14	0.73	0.32	0.74	0.05	0.03	0.00	-2.72
9.	0.34	0.17	0.78	0.34	0.72	0.05	0.03	0.01	-2.62
10.	0.50	0.25	0.85	0.36	0.50	0.05	0.06	0.01	-2.21
11.	0.74	0.37	0.95	0.41	0.26	0.03	0.09	0.01	-1.92
12.	0.81	0.40	0.97	0.34	0.19	0.03	0.12	0.03	-1.57

TABLE-XVII (Contd.)

Sl. No.	$\overline{X}_{Mg}$	$\overline{m}_{Mg}$	X_{Mg}	m_{Mg}	$\overline{X}_H=\overline{m}_H$	$X_H=m_H$	α_H^{Mg}	K_c	log K_c
					At 50°C				
1.	0.09	0.05	0.13	0.06	0.86	0.49	0.41	0.22	-0.65
2.	0.14	0.07	0.25	0.13	0.84	0.41	0.26	0.12	-0.91
3.	0.16	0.08	0.38	0.19	0.83	0.31	0.16	0.06	-1.22
4.	0.17	0.09	0.51	0.26	0.52	0.28	0.12	0.04	-1.42
5.	0.20	0.10	0.59	0.30	0.81	0.25	0.10	0.03	-1.52
6.	0.21	0.11	0.66	0.34	0.80	0.22	0.09	0.02	-1.63
7.	0.25	0.12	0.69	0.31	0.80	0.20	0.09	0.03	-1.60
8.	0.29	0.15	0.73	0.32	0.75	0.06	0.03	0.003	-2.56
9.	0.35	0.18	0.78	0.34	0.71	0.05	0.03	0.003	-2.51
10.	0.45	0.23	0.82	0.35	0.68	0.05	0.04	0.004	-2.41
11.	0.76	0.38	0.95	0.39	0.24	0.03	0.11	0.02	-1.77
12.	0.82	0.41	0.97	0.33	0.18	0.03	0.15	0.04	-1.43

TABLE - XVIII

EQUIVALENT IONIC FRACTIONS, SEPARATION FACTORS, MOLALITIES AND SELECTIVITY COEFFICIENTS FOR THE Ca(II) - H(I) EXCHANGE ON ANTIMONY(V) SILICATE CATION EXCHANGER

Sl. No.	$\overline{X}_{Ca}$	$\overline{m}_{Ca}$	X_{Ca}	m_{Ca}	$\overline{X}_H=\overline{m}_H$	$X_H=m_H$	α_H^{Ca}	K_C	log K_c
				At 25°C					
1.	0.15	0.08	0.02	0.01	0.71	0.94	13.34	14.11	1.15
2.	0.25	0.13	0.03	0.01	0.64	0.94	14.84	20.09	1.30
3.	0.41	0.20	0.04	0.02	0.48	0.87	21.34	37.54	1.57
4.	0.55	0.28	0.06	0.03	0.39	0.79	19.93	39.87	1.60
5.	0.67	0.33	0.13	0.06	0.38	0.75	10.60	21.14	1.33
6.	0.72	0.36	0.25	0.13	0.35	0.71	5.77	11.68	1.07
7.	0.74	0.37	0.35	0.18	0.32	0.66	4.41	9.20	0.96
8.	0.74	0.37	0.45	0.23	0.29	0.66	3.81	8.66	0.94
9.	0.75	0.38	0.60	0.31	0.26	0.51	2.42	4.54	0.66
10.	0.76	0.38	0.70	0.37	0.23	0.13	0.62	0.34	-0.46
11.	0.79	0.39	0.75	0.38	0.23	0.13	0.61	0.34	-0.47
12.	0.84	0.42	0.82	0.42	0.17	0.13	0.78	0.58	-0.24

TABLE-XVIII (Contd.)

Sl. No.	$\overline{X}_{Ca}$	$\overline{m}_{Ca}$	X_{Ca}	m_{Ca}	$\overline{X}_H = \overline{m}_H$	$X_H = m_H$	α_H^{Ca}	K_c'	log K_c
					At 50°C				
1.	0.29	0.15	0.01	0.01	0.71	0.99	40.93	56.33	1.75
2.	0.42	0.21	0.01	0.01	0.58	0.99	71.14	118.99	2.08
3.	0.50	0.25	0.02	0.01	0.44	0.99	55.48	122.78	2.01
4.	0.66	0.33	0.04	0.02	0.41	0.98	45.26	110.01	2.04
5.	0.70	0.35	0.05	0.02	0.30	0.95	45.19	148.12	2.17
6.	0.74	0.37	0.11	0.05	0.26	0.89	22.58	77.84	1.89
7.	0.77	0.38	0.26	0.13	0.24	0.82	10.23	35.76	1.55
8.	0.78	0.39	0.45	0.23	0.22	0.74	5.95	20.17	1.30
9.	0.80	0.40	0.62	0.31	0.20	0.66	4.16	13.28	1.12
10.	0.82	0.41	0.74	0.37	0.16	0.18	1.24	1.35	0.13
11.	0.84	0.42	0.80	0.41	0.13	0.16	1.35	1.81	0.26
12.	0.86	0.43	0.84	0.43	0.08	0.15	1.83	3.19	0.50

TABLE - XIX

EQUIVALENT IONIC FRACTIONS, SEPARATION FACTORS, MOLALITIES AND SELECTIVITY COEFFICIENTS FOR THE Sr(II) - H(I) EXCHANGE ON ANTIMONY(V) SILICATE CATION EXCHANGER

Sl. No.	$\overline{X}_{Sr}$	$\overline{m}_{Sr}$	X_{Sr}	m_{Sr}	$\overline{X}_H=\overline{m}_H$	$X_H=m_H$	α_H^{Sr}	K_c	log K_c
				At 25°C					
1.	0.27	0.13	0.01	0.005	0.73	0.99	36.62	47.82	1.68
2.	0.40	0.20	0.02	0.01	0.60	0.98	32.67	53.36	1.73
3.	0.48	0.24	0.04	0.02	0.52	0.96	22.15	40.90	1.61
4.	0.54	0.27	0.26	0.09	0.46	0.74	3.34	7.76	0.89
5.	0.59	0.29	0.14	0.05	0.41	0.86	8.84	25.52	1.41
6.	0.61	0.30	0.20	0.07	0.39	0.80	6.26	7.81	0.89
7.	0.67	0.33	0.39	0.14	0.33	0.61	3.18	8.05	0.91
8.	0.74	0.37	0.55	0.20	0.26	0.45	2.33	5.54	0.74
9.	0.78	0.39	0.68	0.25	0.22	0.32	1.67	3.30	0.52
10.	0.81	0.40	0.73	0.27	0.19	0.27	1.58	2.99	0.48
11.	0.92	0.46	0.79	0.29	0.08	0.20	2.91	9.91	1.00
12.	0.95	0.47	0.83	0.30	0.05	0.17	3.89	18.11	1.26

TABLE-XIX (Contd.)

Sl. No.	$\overline{X}_{Sr}$	$\overline{m}_{Sr}$	X_{Sr}	m_{Sr}	$\overline{X}_H=\overline{m}_H$	$X_H=m_H$	α_H^{Sr}	K_c	log K_c
					At 50°C				
1.	0.28	0.14	0.01	0.005	0.72	1.00	38.87	54.01	1.73
2.	0.41	0.20	0.02	0.01	0.59	0.98	34.05	55.18	1.74
3.	0.51	0.25	0.03	0.015	0.49	0.97	33.65	65.31	1.82
4.	0.61	0.30	0.12	0.05	0.39	0.88	11.47	30.55	1.48
5.	0.68	0.34	0.20	0.08	0.32	0.80	8.50	26.56	1.42
6.	0.76	0.38	0.25	0.10	0.24	0.75	9.50	37.11	1.57
7.	0.86	0.43	0.37	0.13	0.14	0.63	10.46	66.98	1.83
8.	0.91	0.45	0.55	0.19	0.10	0.45	7.44	47.96	1.68
9.	0.92	0.46	0.70	0.25	0.08	0.30	4.93	25.88	1.41
10.	0.93	0.46	0.73	0.26	0.05	0.27	6.88	51.59	1.71
11.	0.97	0.48	0.78	0.28	0.03	0.20	8.29	76.19	1.88
12.	0.99	0.49	0.83	0.30	0.02	0.18	10.73	132.3	2.12

TABLE - XX

EQUIVALENT IONIC FRACTIONS, SEPARATION FACTORS, MOLALITIES AND SELECTIVITY COEFFICIENTS FOR THE Ba(II) - H(I) EXCHANGE ON ANTIMONY(V) SILICATE CATION EXCHANGER

Sl. No.	$\overline{X}_{Ba}$	$\overline{m}_{Ba}$	X_{Ba}	m_{Ba}	$\overline{X}_H = \overline{m}_H$	$X_H = m_H$	α_H^{Ba}	K_c	$\log K_c$
				At 25°C					
1.	0.25	0.12	0.02	0.01	0.74	0.98	15.15	15.63	1.19
2.	0.38	0.19	0.05	0.02	0.63	0.94	10.72	17.85	1.25
3.	0.50	0.25	0.15	0.05	0.52	0.91	5.65	15.67	1.20
4.	0.54	0.27	0.23	0.07	0.48	0.82	4.13	11.69	1.07
5.	0.58	0.29	0.37	0.11	0.44	0.74	2.64	7.38	0.87
6.	0.60	0.30	0.51	0.15	0.42	0.66	1.84	4.81	0.68
7.	0.60	0.30	0.58	0.17	0.40	0.60	1.57	3.71	0.57
8.	0.60	0.30	0.67	0.20	0.38	0.55	1.31	3.13	0.50
9.	0.62	0.31	0.75	0.23	0.36	0.51	1.15	2.62	0.42
10.	0.65	0.32	0.83	0.26	0.33	0.15	0.33	0.25	-0.60
11.	0.70	0.35	0.85	0.26	0.30	0.13	0.35	0.24	-0.62
12.	0.76	0.38	0.86	0.26	0.24	0.13	0.46	0.39	-0.41

TABLE - XX (Contd.)

Sl. No.	$\overline{X}_{Ba}$	$\overline{m}_{Ba}$	X_{Ba}	m_{Ba}	$\overline{X}_H=\overline{m}_H$	$X_H=m_H$	α^{Ba}_{H}	K_c	log K_c
				At 50°C					
1.	0.24	0.12	0.01	0.006	0.75	0.99	31.52	33.60	1.53
2.	0.41	0.20	0.04	0.02	0.64	0.99	17.64	22.25	1.35
3.	0.46	0.23	0.07	0.03	0.54	0.93	1.12	26.23	1.42
4.	0.53	0.26	0.15	0.05	0.50	0.86	5.90	16.70	1.22
5.	0.61	0.31	0.30	0.09	0.47	0.77	3.27	9.03	0.96
6.	0.62	0.31	0.41	0.12	0.44	0.71	2.46	6.69	0.83
7.	0.64	0.32	0.50	0.15	0.42	0.64	1.91	4.98	0.70
8.	0.64	0.32	0.60	0.18	0.40	0.60	1.59	3.96	0.60
9.	0.65	0.32	0.70	0.21	0.37	0.57	1.44	3.65	0.56
10.	0.69	0.35	0.81	0.25	0.29	0.15	0.44	0.36	-0.44
11.	0.76	0.38	0.85	0.26	0.27	0.15	0.49	0.44	-0.36
12.	0.78	0.39	0.86	0.26	0.22	0.14	0.56	0.56	-0.25

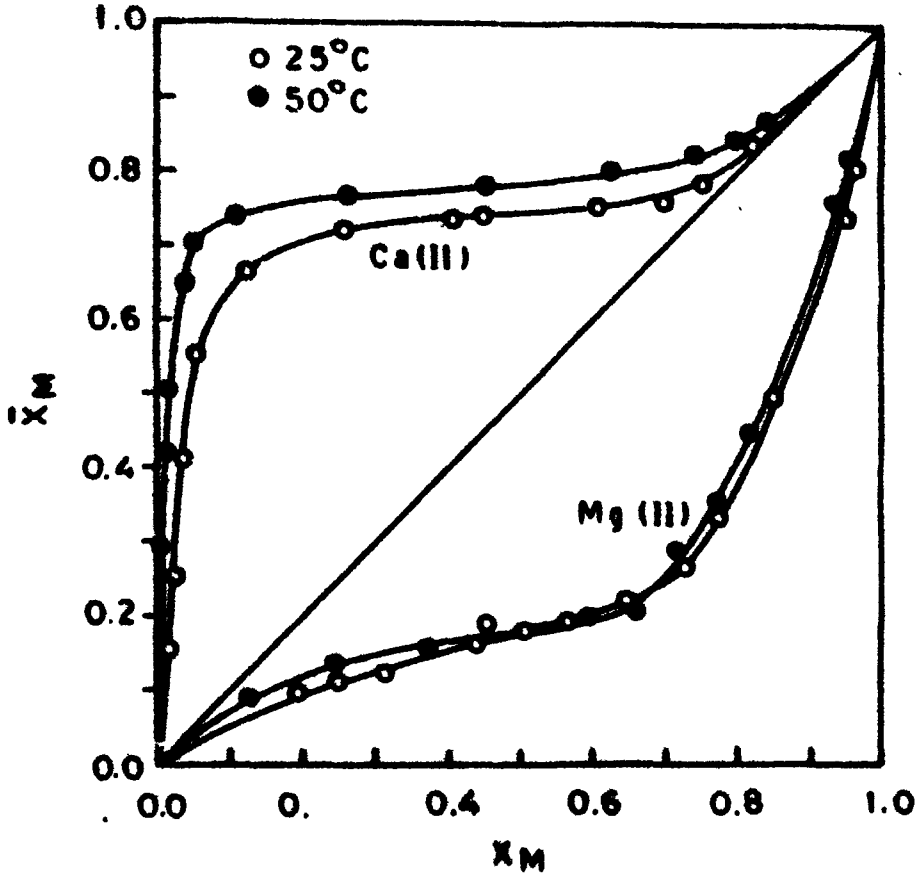

FIG. 24 EXCHANGE ISOTHERMS OF THE Mg(II)-H(I) AND Ca (II)-H(I) EXCHANGES ON ANTIMONY(V)SILICATE AT 25° AND 50°C

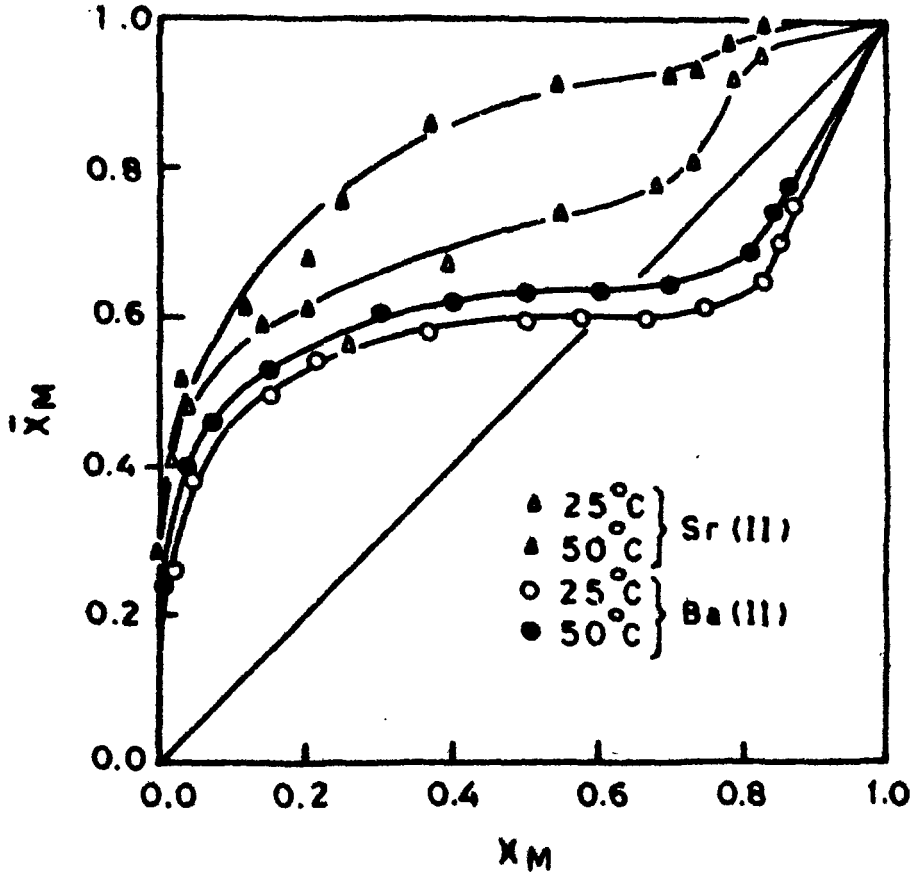

FIG.25 EXCHANGE ISOTHERMS OF THE Sr(II)-H(I) AND Ba(II)-H(I) EXCHANGES ON ANTIMONY(V) SILICATE AT 25° AND 50°C

In Ba(II) - H(I) exchange the isotherms are sigmoid indicating a selectivity reversal at both the temperatures. It means that Barium ions are preferred by the exchanger upto a certain value of the ionic fraction (0.60 at 25° and 0.64 at 50°C), thereafter, a preference for H(I) ions is shown. This conclusion is substantiated by the values of the separation factors and selectivity coefficients (Tables XVII to XX).

The thermodynamic equilibrium constants (K) were determined (22) from the relationship:

$$\ln K = (Z_A - Z_B) + \int_0^1 \ln K_c \, d\bar{X}_M \qquad \text{- - - - - - - (5)}$$

where Z_A and Z_B are the valencies of the competing ions. The integrals were evaluated from the areas under the curves of Figures 26 and 27 using the trapazoidal rule (23). The K values are given in Table XXI. A comparison of the K values for the different exchanges studied shows the following sequences at the two temperatures:

$$Ca(II) > Sr(II) > Ba(II) > Mg(II) \quad \text{at } 25^\circ C$$

$$Sr(II) > Ca(II) > Ba(II) > Mg(II) \quad \text{at } 50^\circ C$$

which means the same sequence of the affinities for these metal ions. At a higher temperature (50°C) also the affinity is higher for all the exchanges.

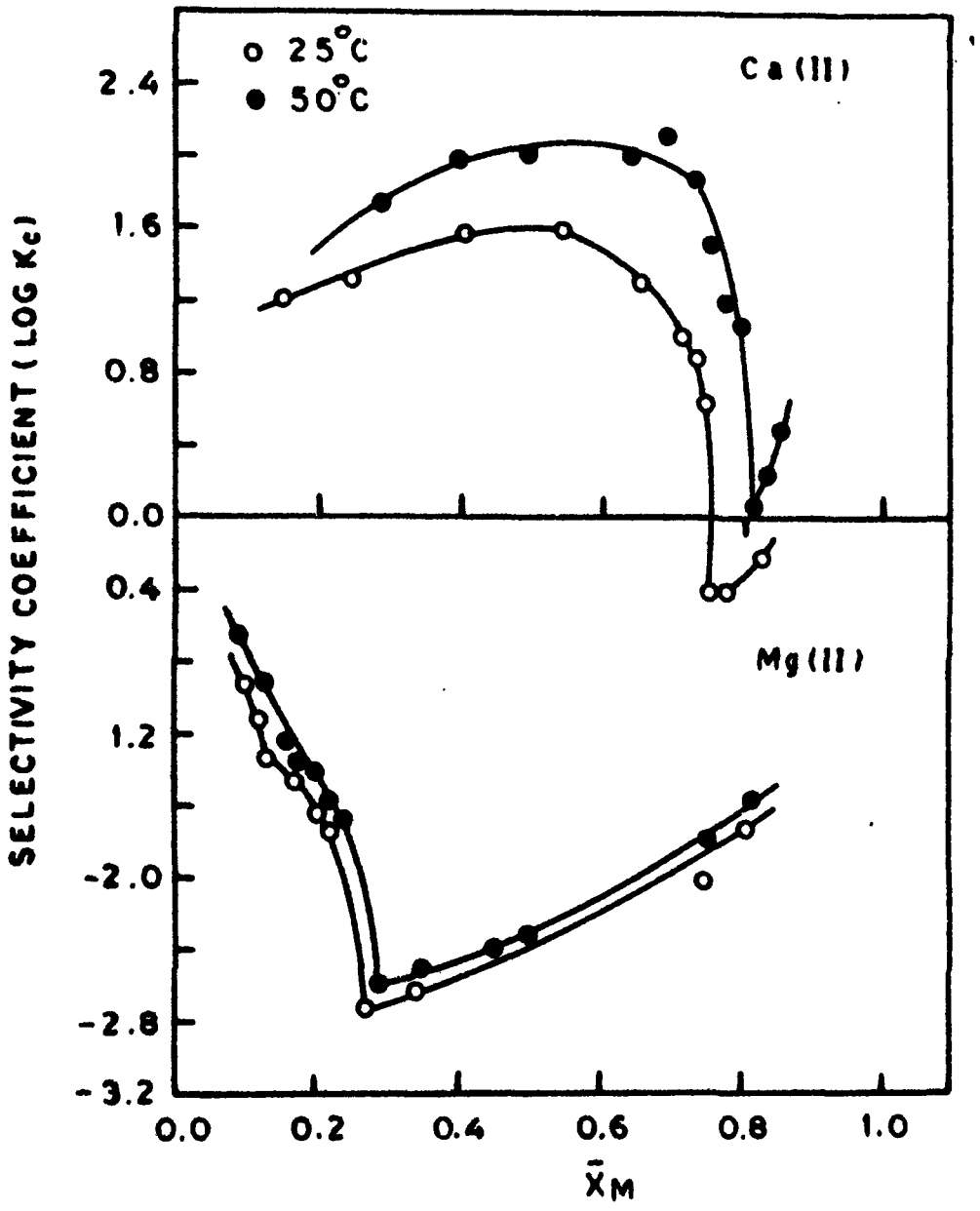

FIG. 26 PLOTS OF LOG K_C VERSUS $\bar{X}_M$ FOR Mg(II) – H(I) AND Ca(II) – H(I) EXCHANGES ON ANTIMONY(V) SILICATE AT 25° AND 50°C

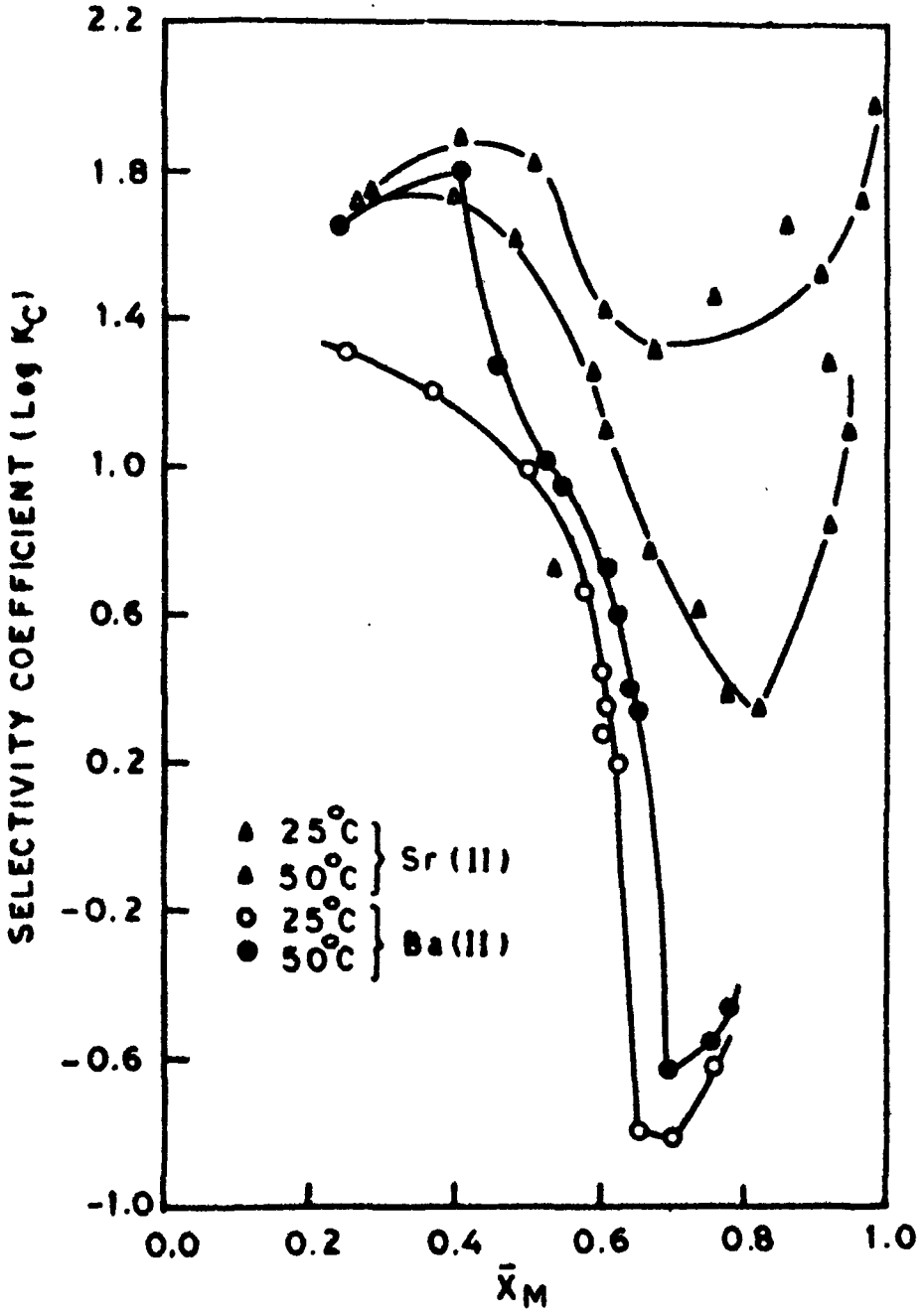

FIG. 27 PLOTS OF LOG K_C VERSUS $\bar{X}_M$ FOR Sr (II) – H(I) AND Ba (II) – H(I) EXCHANGES ON ANTIMONY (V) SILICATE AT 25° AND 50°C

The standard free energies of exchange (ΔG°) for the interaction - 2 were calculated (24) from the relationship:

$$\Delta G^{\circ} = - R T \ln K \qquad \text{----------(6)}$$

where R is universal gas constant and T is the temperature in degrees kelvin.

The standard enthalpy change (ΔH°) were calculated from the Van't Hoff isochare:

$$\ln \left[\frac{K_{T_2}}{K_{T_1}} \right] = - \frac{\Delta H^{\circ}}{R} \left(\frac{I}{T_2} - \frac{I}{T_1} \right) \qquad \text{-------(7)}$$

and standard entropy change (ΔS°) by the following equation:

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \qquad \text{--------(8)}$$

Table XXI also summarizes the values of ΔG°, ΔH° and ΔS°.

A positive value of ΔG° for the Mg(II) - H(I) interaction at both the temperatures indicates that SbSi has a lower preference for Mg(II) than for H(I) at both the temperatures. However, in case of the Ca(II), Sr(II) and Ba(II) exchanges with H(I) ions the reverse is true i.e. the negative standard free energy change for these interactions means that these metal ions are preferably adsorbed on SbSi than H(I) ions and the preference increases at a higher

temperature. A positive enthalpy change in these interactions also confirms this view. Positive values of standard entropy change suggest that the metal ions are less strongly bound with the exchanger as compared to the H(I) ions.

The activity coefficients of the metal and H(I) ions were calculated (25,26) from the following expressions:

$$\ln f_M = (\bar{X}_M - 1) \ln K_c - \int_0^{\bar{X}_M} \ln K_c \, d\bar{X}_M \qquad \text{- - - - - - - - (9)}$$

$$\ln f_H = \bar{X}_M \ln K_c - \int_0^{\bar{X}_M} \ln K_c \, d\bar{X}_M \qquad \text{- - - - - - - - (10)}$$

and the values are tabulated in Tables XXI to XXV.

In Ca(II) - H(I), Sr(II), H(I) and Ba(II) - H(I) exchanges the f_M values are less than unity at both the temperatures. However, in the Mg(II) - H(I) exchange the values are greater than unity and generally increase with the increase in the $\bar{X}_{Mg}$ values at both the temperatures. Further, a variation of f_H values is observed in all the cases indicating a heterogeneity in the distribution of ions on SbSi surface during the ion-exchange process, similar to the others reported earlier (27). Soils also behave similarly (28).

To further examine the deviation of these heterogeneous systems from ideality, the excess thermodynamic functions for these systems were calculated (29,30) from the expressions:

$$\Delta G^{x}_{m} = RT \left[\bar{X}_M \ln f_M + \bar{X}_H \ln f_H \right] \quad \text{- - - - - - - - - (11)}$$

$$\Delta H^{x}_{m} = RT^2 \left[\bar{X}_M \left(\frac{\ln f_M}{T} \right) + \bar{X}_H \left(\frac{\ln f_H}{T} \right) \right] \quad \text{- - - - (12)}$$

and $$\Delta G^{x}_{m} = \Delta H^{x}_{m} - T\Delta S^{x}_{m} \quad \text{- - - - - - - - - (13)}$$

where ΔG^{x}_{m}, ΔH^{x}_{m} and ΔS^{x}_{m} are the excess free energies, enthalpies and entropies of mixing (Tables XXVI to XXIX). It is clear from these tables that the values of the excess free energy change are positive for the Mg(II) - H(I) exchange and increase with the increase in the values of $\bar{X}_{Mg}$. However for the Ca(II) - H(I), Sr(II) - H(I) and Ba(II) - H(I) exchanges the values of ΔG^{x}_{m} are negative at both the temperatures studied, indicating that the heterogenous mixtures of Ca(II) - H(I), Sr(II) - H(I) and Ba(II) - H(I) ions during the exchange are more stable as compared to the pure homoionic forms. The reverse is true for the Mg(II) - H(I) exchange.

The enthalpies and entropies of mixing for the Ca(II) - H(I) exchange are negative upto certain limit ($\bar{X}_{Ca}$ = 0.72 and 0.70 at 25° and 50°C respectively). Thereafter, the values are positive. This reversal in the signs indicates a higher binding strength of the ion-mixture as compared to a single ion. In case of the Mg(II) - H(I) exchange, however, no definite order is found. It is in accordance with the work of Howery and Thomas (26) for the ion exchange on the mineral clinoptilotite. A comparison of these values at both the temperatures suggests that Ca(II) and Sr(II) are the most strongly bound ions at 25° and 50°C respectively.

TABLE - XXI

VALUES OF SOME THERMODYNAMIC PARAMETERS FOR THE Mg(II) - H(I), Ca(II) - H(I), Sr(II) - H(I) AND Ba(II) - H(I) EXCHANGES ON ANTIMONY(V) SILICATE CATION EXCHANGER

Thermodynamic Parameters	Systems							
	Mg(II) - H(I) at		Ca(II) - H(I) at		Sr(II) - H(I) at		Ba(II) - H(I) at	
	25°C	50°C	25°C	50°C	25°C	50°C	25°C	50°C
K	0.07	0.12	18.33	25.96	13.68	26.95	5.35	6.64
ΔG° (KJ mole^{-1})	6.70	5.63	-7.22	-8.76	-6.49	-8.89	-4.17	-5.09
ΔH° (KJ mole^{-1})	19.45		11.13		21.73		6.87	
ΔS° (KJ mole^{-1} deg^{-1})	0.04	0.04	0.06	0.06	0.09	0.09	0.04	0.04

TABLE - XXII

ACTIVITY COEFFICIENTS FOR THE DIFFERENT $\overline{X}_{Mg}$ VALUES IN THE Mg(II)-H(I) EXCHANGE ON ANTIMONY(V) SILICATE CATION EXCHANGER

Sl. No.	Values at 25°C			Values at 50°C		
	$\overline{X}_{Mg}$	f_{Mg}	f_H	$\overline{X}_{Mg}$	f_{Mg}	f_H
1.	0.10	6.65	0.82	0.09	3.87	0.88
2.	0.12	11.05	0.75	0.14	6.18	0.78
3.	0.13	16.39	0.71	0.16	11.06	0.65
4.	0.17	19.95	0.68	0.18	11.66	0.69
5.	0.19	20.62	0.66	0.20	19.84	0.63
6.	0.20	29.09	0.61	0.21	25.43	0.62
7.	0.22	32.75	0.58	0.25	23.72	0.53
8.	0.27	208.90	0.35	0.29	137.20	0.33
9.	0.34	177.30	0.39	0.35	142.10	0.38
10.	0.50	117.00	0.61	0.45	104.20	0.36
11.	0.74	94.32	0.94	0.76	49.58	0.71
12.	0.81	86.62	1.56	0.82	42.39	1.10

TABLE - XXIII

ACTIVITY COEFFICIENTS FOR THE DIFFERENT $\overline{X}_{Ca}$ VALUES IN THE Ca(II) - H(I) EXCHANGE ON ANTIMONY(V) SILICATE CATION EXCHANGER

Sl. No.	Values at 25°C			Values at 50°C		
	$\overline{X}_{Ca}$	f_{Ca}	f_H	$\overline{X}_{Ca}$	f_{Ca}	f_H
1.	0.15	0.09	1.52	0.29	0.06	3.19
2.	0.25	0.07	1.62	0.42	0.03	4.16
3.	0.41	0.05	1.95	0.50	0.03	3.27
4.	0.55	0.01	2.00	0.66	0.04	4.07
5.	0.67	0.06	1.36	0.70	0.04	5.40
6.	0.72	0.08	0.89	0.74	0.04	3.18
7.	0.74	0.08	0.76	0.77	0.05	1.88
8.	0.74	0.08	0.73	0.78	0.06	1.00
9.	0.75	0.10	0.45	0.80	0.07	0.88
10.	0.76	0.18	0.09	0.82	0.10	0.14
11.	0.79	0.18	0.22	0.84	0.10	0.18
12.	0.84	0.16	0.10	0.86	0.09	0.29

TABLE - XXIV

ACTIVITY COEFFICIENTS FOR THE DIFFERENT $\overline{X}_{Sr}$ VALUES IN THE Sr(II)-H(I) EXCHANGE ON ANTIMONY(V) SILICATE CATION EXCHANGER

Sl. No.	Values at 25°C			Values at 50°C		
	$\overline{X}_{Sr}$	f_{Sr}	f_H	$\overline{X}_{Sr}$	f_{Sr}	f_H
1.	0.27	0.06	2.81	0.28	0.06	2.99
2.	0.40	0.07	3.72	0.41	0.05	3.88
3.	0.48	0.08	3.31	0.51	0.06	4.11
4.	0.54	0.22	1.17	0.61	0.08	2.09
5.	0.59	0.12	2.26	0.68	0.08	2.99
6.	0.61	0.14	1.76	0.76	0.08	3.61
7.	0.67	0.16	0.94	0.86	0.07	2.08
8.	0.74	0.19	0.77	0.91	0.10	3.49
9.	0.78	0.20	0.49	0.92	0.11	2.03
10.	0.81	0.22	0.48	0.93	0.10	3.84
11.	0.92	0.18	1.35	0.97	0.10	4.59
12.	0.95	0.17	2.13	0.99	0.10	5.90

TABLE - XXV

ACTIVITY COEFFICIENTS FOR THE DIFFERENT $\overline{X}_{Ba}$ VALUES IN THE Ba(II) - H(I) EXCHANGE ON ANTIMONY(V) SILICATE CATION EXCHANGER

Sl. No.	Values at 25°C			Values at 50°C		
	$\overline{X}_{Ba}$	f_{Ba}	f_H	$\overline{X}_{Ba}$	f_{Ba}	f_H
1.	0.25	0.10	2.10	0.24	0.06	2.44
2.	0.38	0.12	1.99	0.41	0.05	3.22
3.	0.50	0.16	1.59	0.46	0.10	1.99
4.	0.54	0.19	1.34	0.53	0.14	1.39
5.	0.58	0.23	1.02	0.61	0.19	1.03
6.	0.60	0.27	0.80	0.62	0.24	0.87
7.	0.60	0.29	0.61	0.64	0.24	0.70
8.	0.60	0.31	0.63	0.64	0.24	0.70
9.	0.62	0.35	0.55	0.65	0.27	0.59
10.	0.65	0.80	0.12	0.69	057	0.13
11.	0.70	0.82	0.12	0.76	0.54	0.15
12.	0.76	0.71	0.35	0.78	0.52	0.18

TABLE - XXVI

EXCESS FREE ENERGIES, ENTHIALPIES AND ENTROPIES OF MIXING FOR THE Mg(II) - H(I) EXCHANGE ON ANTIMONY(V) SILICATE CATION EXCHANGER

Sl. No.	$\overline{X}_{Mg}$	ΔG_m^x (K J mole^{-1})	ΔH_m^x (K J mole^{-1})	ΔS_m^x (K J mole^{-1} deg^{-1})
		At 25°C		
1.	0.10	0.04	3.50	0.01
2.	0.12	0.15	3.18	0.01
3.	0.13	0.22	0.58	0.00
4.	0.17	0.53	2.75	0.01
5.	0.19	0.62	-0.59	0.00
6.	0.20	0.73	1.34	0.00
7.	0.22	0.90	0.06	0.00
8.	0.27	1.64	2.10	0.00
9.	0.34	2.69	2.29	0.00
10.	0.50	5.30	-6.28	-0.06
11.	0.74	8.31	11.87	0.01
12.	0.81	9.19	26.49	0.06

TABLE - XXVI (Contd.)

Sl. No.	$\bar{X}_{Mg}$	ΔG_m^x (KJ mole^{-1})	ΔH_m^x (KJ mole^{-1}	ΔS_m^x (KJ mole^{-1} deg^{-1})
		At 50°C		
1.	0.09	0.03	3.89	0.01
2.	0.14	0.12	3.97	0.01
3.	0.16	0.10	-0.29	0.00
4.	0.18	0.35	3.35	0.01
5.	0.20	0.61	-0.72	0.00
6.	0.21	0.81	1.66	0.00
7.	0.25	0.75	0.22	0.00
8.	0.29	1.63	2.75	0.00
9.	0.35	2.87	3.48	0.00
10.	0.45	3.76	14.52	0.04
11.	0.76	7.78	19.37	0.04
12.	0.82	8.30	22.53	0.04

TABLE - XXVII

EXCESS FREE ENERGIES, ENTHALPIES AND ENTROPIES OF MIXING FOR THE Ca(II) - H(I) EXCHANGE ON ANTIMONY(V) SILICATE CATION EXCHANGER

Sl. No.	$\overline{X}_{Ca}$	ΔG_m^x (KJ mole^{-1})	ΔH_m^x (KJ mole^{-1})	ΔS_m^x (KJ mole^{-1} deg^{-1})
		At 25°C		
1.	0.15	-0.18	-13.67	-0.05
2.	0.25	-0.87	-12.08	-0.04
3.	0.41	-2.27	0.64	0.01
4.	0.55	-5.63	-29.62	-0.08
5.	0.67	-4.25	- 4.63	-0.00
6.	0.72	-4.71	- 0.27	0.02
7.	0.74	-4.78	0.96	0.02
8.	0.74	-4.83	3.67	0.03
9.	0.75	-4.87	3.67	0.03
10.	0.77	-3.58	7.81	0.04
11.	0.79	-4.17	16.17	0.07
12.	0.84	-4.77	15.01	0.07

TABLE - XXVII (Contd.)

Sl. No.	$\bar{X}_{Ca}$	ΔG_m^x (K J mole^{-1})	ΔH_m^x (KJ mole^{-1})	ΔS_m^x (KJ mole^{-1} deg^{-1})
			At 50°C	
1.	0.29	-0.05	-13.82	-0.04
2.	0.42	-1.55	- 7.96	-0.02
3.	0.50	-3.46	3.33	-0.02
4.	0.66	-4.27	-39.95	-0.11
5.	0.71	-4.88	- 0.93	0.01
6.	0.74	-5.48	3.83	0.03
7.	0.77	-5.68	4.14	0.03
8.	0.78	-5.86	5.47	0.04
9.	0.80	-5.93	6.26	0.04
10.	0.82	-5.88	12.24	0.06
11.	0.84	-5.87	19.48	0.08
12.	0.86	-5.89	14.67	0.06

TABLE - XXVIII

EXCESS FREE ENERGIES, ENTHALPIES AND ENTROPIES OF MIXING FOR THE Sr(II) - H(I) EXCHANGE ON ANTIMONY(V) SILICATE CATION EXCHANGER

Sl. No.	$\overline{X}_{Sr}$	ΔG_m^x (K J mole^{-1})	ΔH_m^x (KJ mole^{-1})	ΔS_m^x (K J mole^{-1} deg^{-1})
		At 25°C		
1.	0.27	-0.05	-0.12	0.00
2.	0.40	-0.69	-2.89	-0.01
3.	0.48	-1.45	0.42	0.01
4.	0.54	-1.87	56.68	0.20
5.	0.59	-2.25	4.11	0.02
6.	0.61	-2.46	0.86	0.01
7.	0.67	-3.10	9.14	0.04
8.	0.74	-3.22	1.54	0.02
9.	0.78	-3.47	5.03	0.03
10.	0.81	-3.43	5.88	0.03
11.	0.92	-3.78	13.56	0.06
12.	0.95	-4.02	14.20	0.06

TABLE - XXVIII (Contd.)

Sl. No.	$\overline{X}_{Sr}$	ΔG_m^x (KJ mole^{-1})	ΔH_m^x (KJ mole^{-1})	ΔS_m^x (KJ mole^{-} deg^{-1})
		At 50°C		
1.	0.28	-0.05	-1.37	0.00
2.	0.41	-1.13	3.52	0.01
3.	0.51	-1.94	0.99	0.01
4.	0.61	-3.35	77.84	0.25
5.	0.68	-3.69	7.05	0.03
6.	0.76	-4.26	7.38	0.04
7.	0.86	-5.93	21.60	0.09
8.	0.91	-5.20	13.78	0.06
9.	0.92	-5.32	15.79	0.07
10.	0.93	-5.49	20.11	0.08
11.	0.97	-5.85	19.11	0.08
12.	0.99	-6.14	19.62	0.08

TABLE - XXIX

EXCESS FREE ENERGIES, ENTHALPIES AND ENTROPIES OF MIXING FOR THE Ba(II) - H(I) EXCHANGE ON ANTIMONY(V) SILICATE CATION EXCHANGER

Sl. No.	$\overline{X}_{Ba}$	ΔG_m^x (K J mole^{-1})	ΔH_m^x (K J mole^{-1})	ΔS_m^x (K J mole^{-1} deg^{-1})
		At 25°C		
1.	0.25	-0.05	1.07	0.00
2.	0.38	-0.86	1.33	0.01
3.	0.50	-1.66	3.32	0.02
4.	0.54	-1.88	4.74	0.02
5.	0.58	-2.07	3.17	0.02
6.	0.60	-2.16	1.01	0.01
7.	0.60	-2.46	1.69	0.01
8.	0.60	-2.17	3.52	0.02
9.	0.62	-2.17	4.05	0.02
10.	0.65	-2.07	6.26	0.03
11.	0.70	-1.95	6.61	0.03
12.	0.76	-1.27	12.24	0.05

TABLE - XXIX (Contd.)

Sl. No.	$\overline{X}_{Ba}$	ΔG_m^x ($KJmole^{-1}$)	ΔH_m^x ($KJ\ mole^{-1}$)	ΔS_m^x ($KJmole^{-}\ deg^{-1}$)
		At 50°C		
1.	0.24	-0.04	1.02	0.00
2.	0.41	-1.25	2.30	0.01
3.	0.46	-1.81	6.87	0.03
4.	0.53	-3.25	5.38	0.03
5.	0.61	-2.67	3.96	0.02
6.	0.62	-2.53	1.21	0.01
7.	0.64	-2.84	2.08	0.02
8.	0.64	-2.81	4.37	0.02
9.	0.65	-2.83	5.02	0.02
10.	0.69	-2.66	7.91	0.03
11.	0.76	-2.61	8.81	0.04
12.	0.78	-2.43	14.12	0.05

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CHAPTER - V

DISTRIBUTION AND SEPARATION STUDIES OF SOME METAL IONS ON ANTIMONY(V) SILICATE CATION EXCHANGER

Adsorption behaviour of an ion exchanger is an important factor as it determines its utility in the separation field. Inorganic ion exchangers are well known for the separation of metal ions (1), their use being in the nuclear energy industry (2-5) for the separation of selected nuclides such as ^{137}Cs and ^{90}Sr from the wastes of reactor fuels. These materials are of growing interest in relation to the treatment of contaminated water or coolant moderator in reactors working at high temperatures and pressures, as it is generally believed that they are resistant to heat and radiations, silicates are important as they are, in general, temperature resistant, stable under chemical attack and show promising ion exchange behaviour. For example, zirconium silicate is highly selective for alkali metals and alkaline earths (6). Some silica based double salts have also illustrated enhanced ion exchange properties, such as stannic arsenosilicate which is selective for Hg(II) (7). Similarly phosphosilicates of zirconium and titanium have been utilized for the separation of radionuclides (2,8). Since antimony(V) silicate has shown good ion exchange properties in addition to its high thermal and chemical stability as discussed in Chapter II, the following pages summarize a systematic study on its adsorption behaviour for some metal ions. As a result, a few important binary separations have been achieved on its columns.

EXPERIMENTAL

Reagents and chemicals

The antimony pentachloride ($SbCl_5$) was a product of Koch-light Laboratories Ltd. (Colnbrook, Bucks, England). All other reagents and chemicals used in this study were AnalaR grade obtained either from BDH Poole (England) or the E. Merck (Dermstadt).

Radiotracers used

The following nuclides were used as radiotracers with their half life periods shown in perentheses:

^{24}Na(15 hours), ^{42}K(12.5 hours), ^{86}Rb(18.7 days) and ^{137}Cs(30.2 years).

Instrumentation

A waterbath incubator shaker having a temperature variation of $\pm$ 0.5°C was used for the shaking process.

Activity measurements were done in a well type single channel analyser of Electronic Corporation of India Ltd. using a NaI(Tl) detector.

Synthesis of the ion exchange material

Antimony(V) silicate (SbSi) was synthesized as described in Chapter II.

Distribution studies

(a) For common metal ions

250 mg of the exchanger in H^+ form were shaken in an electric shaker at 30 ± 2°C for 4 hours with a 25 ml of the solvent, adjusting the initial metal ion concentration less than 3% of the total ion exchange capacity of the material. The metal ion concentrations in the solution before and after the equilibrium were determined by the standard volumetric method using EDTA as the titrant (9). The distribution coefficient (K_d) for some metal ions in demineralized water (DMW), perchloric acid and DMSO-$HClO_4$ systems are summarized in Table XXX.

(b) For alkali metal ions

The K_d values for Na(I), K(I), Rb(I) and Cs(I) ions were determined using radiotracers by the batch process as follows:

100 mg of the exchanger in H^+ form were taken in a conical flask followed by a 20 ml of the solvent containing 1 ml of the tracer and 1 ml of the carrier solution of the required concentration. The contents were shaken for 4 hours in an electric shaker

for attaining equilibrium. 10 ml of the supernatant liquid were, then, withdrawn for measuring the activity. The standard radioactivity of the tracer solution being known, the K_d values were calculated by the standard formula and shown in Figure 28 at different pH values adjusted with the help of $HClO_4$ of varying concentrations (10^0 to 10^5) and DMW.

The following formula was used for the calculation of the K_d values:

$$K_d = \frac{I - F}{F} \times \frac{V}{m} \quad ml\ g^-$$

where, I = initial volume of the EDTA used or initial activity of the solution

F = final volume of the EDTA used or the final activity of the solution

V = total volume of the solution (ml)

M = mass of the exchanger (g)

Effect of gamma radiations

Antimony(V) silicate was irradiated with the varying doses of gamma radiations (1×10^8, 2×10^8 and 3×10^8 rads) at a dose rate of 0.4M rads/hour using ^{60}Co as a source and $FeSO_4$ as a dosimeter. The K_d values for alkaline earths were then determined as usual on these samples. Table XXXI summarizes the results along with those on the normal sample. Figure 29 shows the trend of variation.

TABLE - XXX

K_d VALUES OF SOME METAL IONS ON ANTIMONY(V) SILICATE IN DIFFERENT SOLVENTS

Sl. No.	Metal Ion	K_d Values						
		DMW	0.01M $HClO_4$	0.1M $HClO_4$	10%HCl+25%DMSO (1 : 20)	10%HCl + 25%DMSO (1 : 10)	10%HCl + 25%DMSO (1 : 5)	10%HCl + 25 % DMSO (1 : 1)
1.	Zn(II)	TA	1800	36	159	39	19	0
2.	Cd(II)	TA	1900	1900	900	900	900	900
3.	Hg(II)	TA	TA	1250	0	0	0	0
4.	Mn(II)	TA	433	14	28	10	0	0
5.	Mg(II)	TA	357	12	33	14	0	0
6.	Ca(II)	TA	TA	TA	1500	1500	1500	357
7.	Sr(II)	TA	TA	TA	TA	1350	1350	480
8.	Ba(II)	TA	TA	1153	1153	616	526	150
9.	Cu(II)	TA	TA	255	220	52	18	0
10.	Ni(II)	TA	900	620	36	20	7	0
11.	VO(II)	TA	866	16	45	32	16	0
12.	Pb(II)	TA	TA	1400	TA	1400	1400	328
13.	Co(II)	TA	655	54	78	54	36	13
14.	Fe(III)	TA	TA	175	633	214	0	0
15.	Al(III)	TA	TA	37	149	44	0	0
16.	Zr(IV)	TA	TA	TA	800	1250	1250	1250
17.	Th(IV)	TA	TA	600	1066	60	218	62
18.	Y(III)	TA	TA	424	TA	424	1203	92
19.	La(III)	TA	TA	572	TA	1000	450	312

TA = Total Adsorption

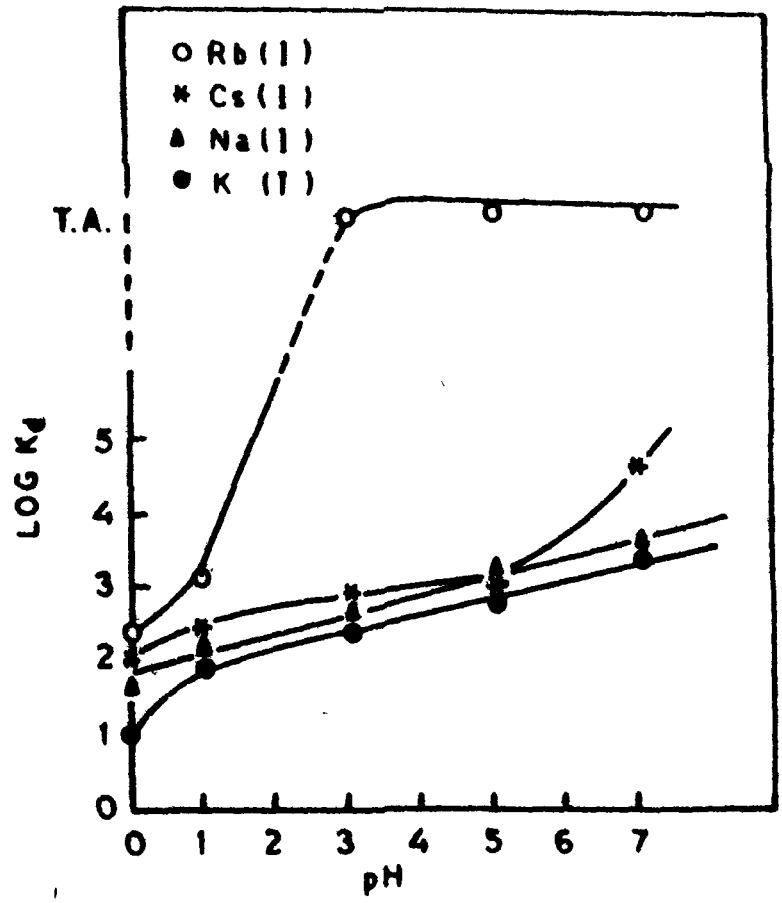

FIG. 28 EFFECT OF pH ON THE K_d VALUES OF ALKALI METALS ON ANTIMONY (V) SILICATE CATION EXCHANGER

TABLE - XXXI

K_d VALUES OF ALKALINE EARTHS ON NORMAL AND IRRADIATED SAMPLES OF ANTIMONY(V) SILICATE CATION EXCHANGER

Sl. No.	Metal Ion	K_d Values											
		DMW				0.01M $HClO_4$				0.1M $HClO_4$			
		Normal Sample	Irradiated with dose (rads)			Normal Sample	Irradiated with dose (rads)			Normal Sample	Irradiated with dose (rads)		
			1×10^8	2×10^8	3×10^8		1×10^8	2×10^8	3×10^8		1×10^8	2×10^8	3×10
1.	Mg(II)	962	620	670	670	183	200	156	196	30	40	20	50
2.	Ca(II)	4550	4550	5775	5775	3700	4550	5775	1466	675	675	370	370
3.	Sr(II)	2025	2025	4150	4150	1320	2025	4150	1600	203	88	370	13
4.	Ba(II)	4900	4900	6150	6150	1566	1566	6150	6150	1150	1560	1560	1500

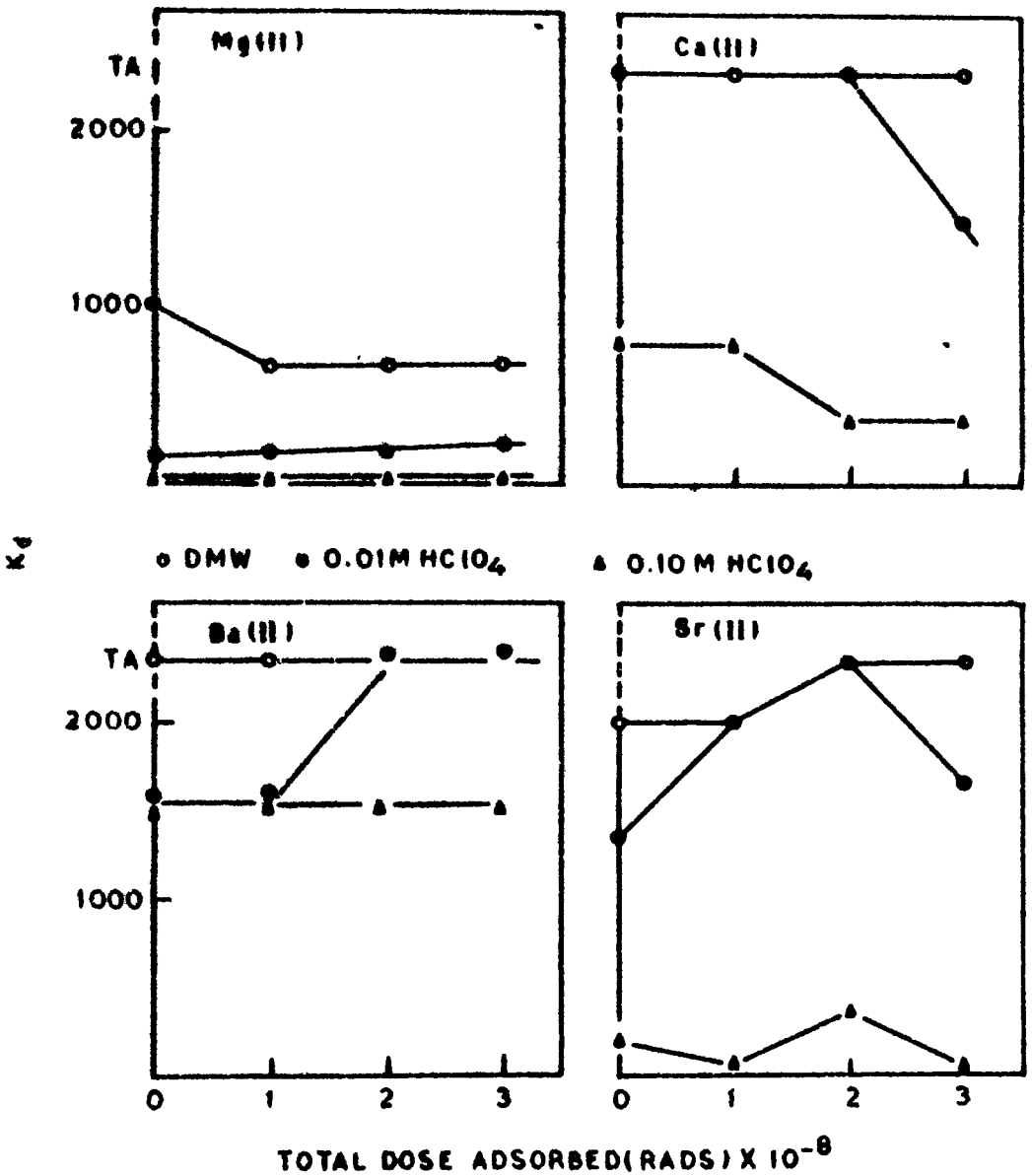

FIG. 29 PLOTS OF K_d VERSUS TOTAL DOSE OF GAMMA RADIATIONS ON ANTIMONY(V)SILICATE

Separations achieved

Several binary separations were tried using a column of i.d. $\sim$ 0.6 cm containing 2 g of the 50 - 70 mesh size exchanger beads in H^+ form. The column was washed thoroughly with DMW and the mixture to be separated was adsorbed on its top. It was eluted out with a suitable solvent at a flow rate $\sim$ 0.5 ml/min. The solvent was selected on the basis of the K_d values and the determination of metal ions was made by EDTA titrations. Table XXXII summarizes the important separations achieved on the columns of antimony(V) silicate with their salient features while Figures 30-32 show the elution curves. The limits of separations were determined on the basis of the permissible error range as $\pm$ 5% .

The height equivalent to a theoretical plate (HETP) was calculated (10) using the formula:

$$HETP = \frac{Lb^2}{8V_{max}^2}$$

where L is the column height (7.0 cm) b is the peak width (ml) at a height of 0.369 C_{max} and V_{max} is the eluant volume (ml) at the peak.

TABLE - XXXII

SOME BINARY SEPARATIONS OF METAL IONS ACHIEVED ON ANTIMONY(V) SILICATE COLUMNS

Sl. No.	Separation achieved	Amount loaded (µg)	Amount found (µg)	% Error	Eluant used	Volume of eluant used (ml)	HETP (Cm)
1.	Zn(II) - Cd(II)	200 Zn	200 Zn	0.0	0.1M $HClO_4$	50	1.72
		304 Cd	309 Cd	+1.6	1.0M $HClO_4$	30	-
2.	Mn(II) - Cd(II)	71 Mn	67 Mn	-5.6	0.1M $HClO_4$	80	3.50
		187 Cd	187 Cd	0.0	1.0M $HClO_4$	60	-
3.	Hg(II) -Pb(II)	240 Hg	240 Hg	0.0	10% $HClO_4$ + 5% DMSO	40	1.37
		517 Pb	497 Pb	-3.8	1.0M $HClO_4$	40	-
4.	Mg(II) - Ca(II)	34 Mg	35 Mg	+2.6	0.1M $HClO_4$	70	3.86
		64 Ca	64 Ca	0.0	1.0M $HClO_4$	40	-
5.	Mg(II) - Sr(II)	48 Mg	49 Mg	+2.0	0.1M $HClO_4$	80	4.24
		123 Sr	123 Sr	0.0	1.0M $HClO_4$	30	-
6.	Mg(II) - Ba(II)	34 Mg	34 Mg	0.0	0.1M $HClO_4$	60	2.24
		112 Ba	112 Ba	0.0	1.0M $HClO_4$	30	-

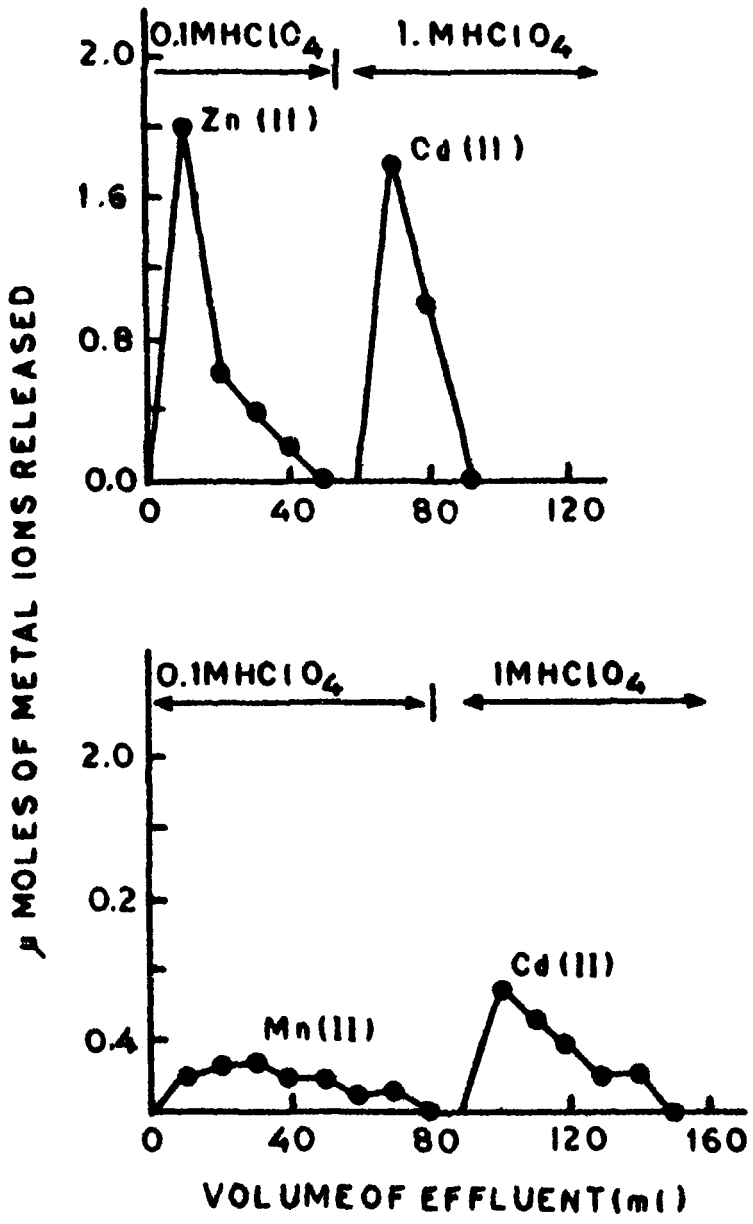

FIG. 30 ELUTION CURVES SHOWING THE SEPARATION OF Cd (II) FROM Zn(II) AND Mn (II) ON ANTIMONY (V) SILICATE COLUMNS

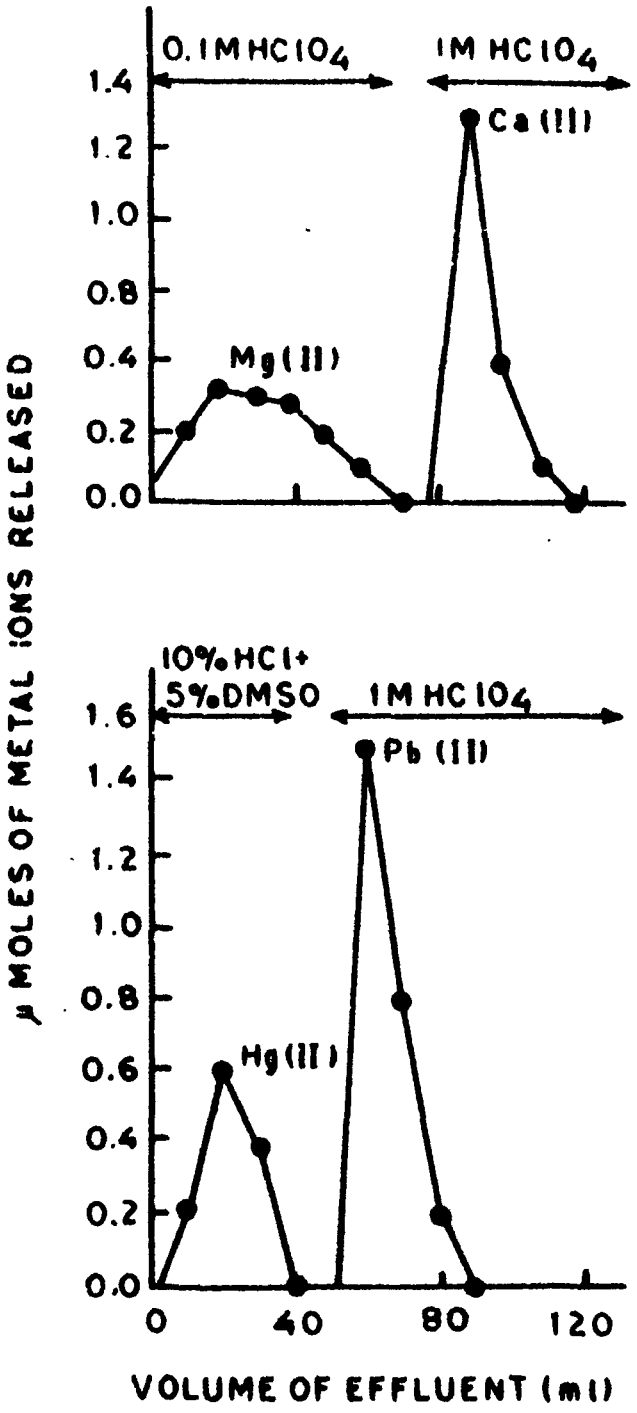

FIG. 31 ELUTION CURVES SHOWING THE SEPARATIONS OF Mg (II) – Ca (II) AND Hg (II) – Pb (II) ON ANTIMONY (V) SILICATE COLUMNS

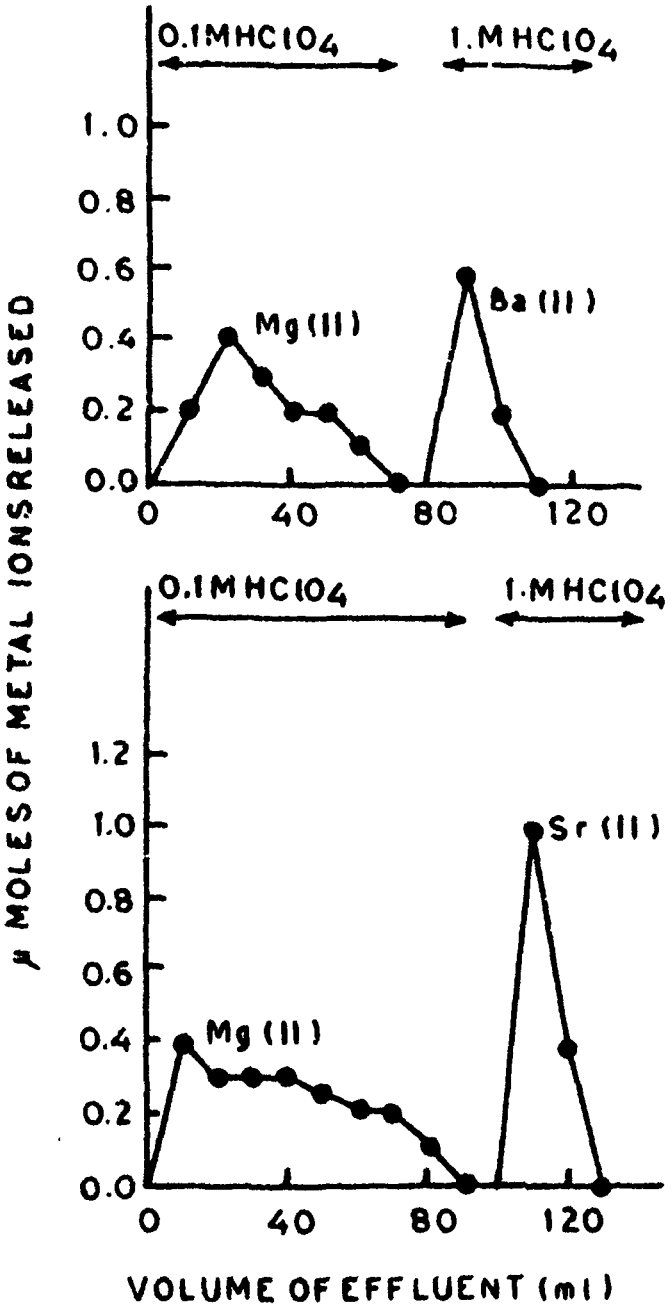

FIG. 32 ELUTION CURVES SHOWING THE SEPARATION OF Mg(II) FROM Sr(II) AND Ba(II) ON ANTIMONY(V) SILICATE COLUMNS

DISCUSSION

The distribution studies illustrate certain interesting features of antimony(V) silicate. Plots of pH versus log K_d for alkali metals (Figure 28) show that they are straight lines for Na(I) and K(I) only. It shows a positive deviation for Cs(I) above pH 5 and a total absorption for Rb(I) at pH $\geqslant 3$. These observations point out the suitability of antimony(V) silicate cation exchanger for the separation of Rb(I) from other alkali metals. Effect of gamma radiations was seen on the distribution behaviour of this material for alkaline earths (Figure 29). As it is clear from this figure the gamma irradiation lowers the K_d values of Ca(II) and Sr(II) while the values for Mg(II) and Ba(II) are not affected significantly in $HClO_4$ medium.

The utility of this material has been demonstrated by achieving separations of great analytical importance. For example Mg(II) has been separated from other alkaline earths. Also, the most difficult separation of Cd(II) from Zn(II) has been performed on its column with a single eluant 1M $HClO_4$. Although antimonic acid has earlier shown (11) a great affinity for Cd(II), a separation of Cd(II) from Zn(II) could not be achieved on its column. For this reason antimony(V) silicate has an added advantage over antimonic acid. Figures 30 to 32 illustrate the six binary separa-

tions achieved on SbSi columns such as Zn(II) - Cd(II), Mn(II) - Cd(II), Hg(II) - Pb(II), Mg(II) - Ca(II), Mg(II) - Sr(II) and Mg(II) - Ba(II). Table XXXII gives the essential features of these separations with the HETP values which signify the column efficiency.

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CHAPTER - VI

A SELECTIVE AND SENSITIVE SPOT TEST METHOD FOR THE DETECTION OF IRON(III) AND MOLYBDENUM(VI) ON ANTIMONY(V) SILICATE BEADS

Several spot tests are known (1,2) for iron and molybdenum, some of which are quite selective and sensitive (3,4). Resin spot tests were introduced by Fujimoto (5) who noticed that the sensitivity and stability of a spot test are greatly enhanced by this technique. Inorganic ion exchangers have been found useful for the metal separations (6) and have been utilized for the analysis of some standard samples of alloys and silicate rocks (7,8). However, their use in the spot test analysis of metal ions is not yet widely known. Antimony(V) silicate is found as a crystalline material with promising cation exchange properties. The present chapter describes a sensitive and selective detection procedure of iron(III) and molybdenum(VI) using antimony(V) silicate beeds as an adsorbent and sodium diethyl dithiocarbamate as a reagent.

EXPERIMENTAL

Reagents and chemicals

Antimony(V) chloride was a Kochlight product and sodium silicate was a Riedal product. Sodium diethyl dithiocarbamate and all other chemicals were of BDH (England) or AnalaR grade.

Synthesis of antimony(V) silicate (SbSi)

SbSi was prepared by the same process as described in Chapter II.

Preparation of the reagent solution

Decimolar solution of sodium diethyl dithiocarbamate was prepared in 100 ml of demineralized water (DMW).

Detection procedure

Few antimony(V) silicate beads (100-150 mesh size) in H^+ form were placed on a spot plate followed by a drop (0.01 ml) of the metal solution and a drop of the reagent solution. Appearence of a brown colour on the beads within 2 minutes indicates the presence of Fe(III). For Mo(VI) the beads turn yellowish pink. The limit of detection was 0.1 µg for both the metal ions.

Study of interferences in the detection procedure

(a) The following ions do not interfere with the test for iron(II) and molybdenum(VI) upto the amounts shown against them in micrograms:

Li(I)(6.94), Na(I)(23.0), K(I)(39.1), Zn(II)(65.4), Cd(II)(112.4), Mn(II)(54.9), Hg(II)(200.6), Pb(II)(207.2), Mg(II)(24.3), Ca(II) (40.1), Sr(II)(87.6), Ba(II)(137.4), Al(III)(27.0), Cr(III)(52.0), Sn(IV)(118.7), Zr(IV)(91.2), Th(IV)(232.0), Ce(IV)(140.1), F^-(19.0), Cl^-(35.5), Br^-(80.0), I^-(126.9), NO_3^-(62.0), CH_3COO^-(59.0), HSO_4^- (58.0), $C_2O_4^{--}$(88.0), $S_2O_3^{--}$ (80.0), MnO_4^-(119.0), $Cr_2O_7^{--}$ (216.0).

(b) The following metal ions give colour noted against them, on the beads when they are present in the amounts greater than shown in brackets:

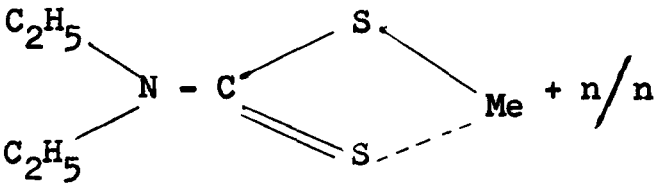
Cu(II)(0.1 µg) - Y, Ni (II)(0.6 µg) - LY, Co(II)(0.06 µg) - LG, Bi(III) (2.1 µg) - LY, Ag(I)(10.8 µg) - LB, U(VI)(1 µg) - LY and W(VI)(18.4 µg) - LO.

Abbreviations used:

Y - Yellow, LY - Light Yellow, LG - Light Green,
LB - Light Brown, LO - Light Orange.

DISCUSSION

Diethyl dithiocarbamate is a commonly known (17) complexing ion and forms metal complexes of the type (18):



Since antimony(V) sulphide has earlier been reported (19) as an excellent collector for Mo(VI), and since antimony(V) silicate prepared in these studies has shown a high selectivity for Fe(III) and Mo(VI), the presence of Sb(V) is probably the key factor to provide an ideal base for the detection of these two metal ions. Some inorganic ion exchangers were also tried (Table XXXIII) for comparison out of which only SbSi gives the best result in terms of the sensitivity of the test. Thorium oxide does not give any positive test probably because it is an anion exchanger while the complexes formed are positively charged. Same is the observation with an organic resin (Dowex - 50 or Amberlite IR-120). A negative test with the organic resins may be attributed to their true ion exchange behaviour as against the inorganic materials which show adsorption as well as ion exchange phenomena occurring on their surfaces.

TABLE - XXXIII

DETECTION LIMITS FOR IRON AND MOLYBDENUM ON DIFFERENT ION EXCHANGE MATERIALS AT ROOM TEMPERATURE (20°C)

Sl. No.	Ion exchange materials	Amount of Iron and Molybdenum detected per 0.01 ml of the test solution			
		10.0 µg	1.0 µg	0.5 µg	0.1 µg
1.	Antimony(V) silicate	+	+	+	+
2.	Antimonic(V) acid (9)	+	+	+	-
3.	Thorium(V) oxide (10)	-	-	-	-
4.	Thorium(IV) phospho-silicate (11)	+	-	-	-
5.	Tin(IV) phosphate (12)	+	-	-	-
6.	Tin(IV) phosphosilicate (13)	+	+	-	-
7.	Tin(IV) arsenate (14)	+	-	-	-
8.	Tin(IV) arsenosilicate (15)	+	+	-	-
9.	Zirconium(IV) phospho-silicate (16)	+	-	-	-
10.	Zirconium(IV) arseno-silicate (7)	+	-	-	-
11.	Zirconium(IV) arseno-phosphate (8)	+	-	-	-
12.	Dowex - 50	-	-	-	-
13.	Amberlite IR-120	-	-	-	-

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Cation-Exchange Study on a Crystalline and Thermally Stable Phase of Antimony Silicate. Effect of Irradiation on Ion-Exchange Behavior and Separation of Cd(II) from Zn(II) and Mn(II) and of Mg(II) from Ba(II), Ca(II), and Sr(II)

K. G. VARSHNEY, UMA SHARMA, SIMA RANI, and A. PREMADAS

CHEMISTRY SECTION
Z H COLLEGE OF ENGINEERING AND TECHNOLOGY
ALIGARH MUSLIM UNIVERSITY
ALIGARH 202001 INDIA

Abstract

A systematic ion-exchange study has been performed on antimony silicate, which includes its ion-exchange capacity, elution behavior, pH titrations, and distribution coefficients of common metal ions The K_d values for alkali metals vary with the pH of the solution and the material is found to be highly selective for Rb(I) at pH values greater than 1 On the basis of distribution studies, the separation of Cd(II) from Zn(II) and Mn(II) has been achieved Similarly, Mg(II) has been separated from Ba(II), Ca(II), and Sr(II) to illustrate its utility Antimony silicate is very stable both thermally and chemically and possesses reproducible ion-exchange properties, also, the effect of irradiation on the ion-exchange behavior is negligible A tentative formula of the material has also been proposed based on chemical, infrared, and thermogravimetric analysis studies The x-ray studies reveal that the exchanger is crystalline with a d-value of 6 09 Å

INTRODUCTION

Silicates form one of the most important classes of the ion-exchange materials as they are temperature resistant and stable under chemical attack (*1–4*). Antimony salts such as Zr(IV), Ti(IV), and Sn(IV) antimonates (*5–8*) have received attention because of their reproducible ion-exchange behavior while the antimony-silicon cation exchangers have been prepared and

studied by Novikov and co-workers (*9–13*). However, a systematic ion-exchange study of antimony silicate has been lacking. Our study is summarized in the following pages. The effect of irradiation on the ion-exchange properties of this material is also included.

EXPERIMENTAL

Reagents

The antimony pentachloride used in this study was of ~95% purity obtained from Koch-Light Laboratories Ltd. (Colnbrook, Bucks, England) and the sodium silicate was a Riedal (DEHAENAG, Seelze-Hannover) product. All other reagents and chemicals were of AnalaR grade.

Apparatus

pH measurements were made on an Elico (India) model LI-10 pH meter while infrared studies were performed on a Beckmann IR-20 spectrophotometer. X-ray studies were made on a Philips X-ray unit using a Mo-K_α target, and the radioactivity was measured in a well-type single channel counter of the Electronics Corporation of India Ltd. using a NaI(Tl) detector. A Bausch and Lomb spectronic-20 colorimeter was used for the spectrophotometric studies.

Preparation of the Reagent Solutions

A stock solution (1.0 *M*) of antimony pentachloride was prepared in concentrated HCl and was diluted to the desired concentration with demineralized water (DMW) so that the final concentration of HCl was not less than 4 *M* in the solution. Sodium silicate was dissolved directly in DMW by heating. For distribution studies, the metal salts were also generally dissolved in DMW except the tri- and tetravalent metals for which 2–3 drops of the corresponding acids were necessary to prevent hydrolysis.

Synthesis of the Material

Different samples of antimony silicate were prepared by varying the concentration of the mixing solutions as given in Table 1 and the pH was fixed in the range 0–1 by adding HNO_3 with constant stirring. The gel thus obtained was kept at room temperature (30°C) overnight, filtered, washed

TABLE 1
Preparation of Antimony Silicate (SbSi)

Sample	Concentration of each mixing solution (*M*) ($SbCl_5$ + Na-silicate)	Mixing ratio (Sb Si) by volume	Ion exchange capacity (meq/g)
S-1	0 5	1 1	Unstable in solution
S-2	0 4	1 1	1 6
S-3	0 3	1 1	1 7
S-4	0 2	1 1	1 5
S-5	0 1	1 1	1 7
S-6	0 1	2 2	1 6

with DMW, and dried at 45°C in an air oven. It was then immersed in DMW and the granules were converted into the H^+ form as usual (*14*). On the basis of its apparent chemical stability and general appearance, Sample S-6 was selected for further study. The reproducibility was checked by preparing the samples several times by the same procedure.

Composition

250 mg of the powdered exchanger was fused with ~4 g of Na_2CO_3 in a platinum crucible and transferred in a 100-mL solution of 4 *M* HCl. The amounts of antimony and silica in this solution were determined by standard methods (*15, 16*) and were found to be in the mole ratio 1:3.

Chemical Stability

250 mg of the material was placed in a 25 mL solution of an acid or a base with intermittant shaking for 24 h. The solution was then analyzed for the dissolved antimony and silica content using standard spectrophotometric methods (*17, 18*). The results are shown in Table 2.

Irradiation Studies

Antimony silicate (S-6) was irradiated by γ-rays obtained from a ^{60}CO source for 96 h under a dose rate of 0.4 Mrd/h using $FeSO_4$ as the dosimatter.

TABLE 2
Chemical Stability of SbSi

Solvent	Amount dissolved in (mg) per 25 mL	
	Sb	Si
1 *M* HNO_3	0 65	0 00
2 *M* HNO_3	2 34	0 00
4 *M* HNO_3	2 95	0 07
1 *M* HCl	1 31	0 00
2 *M* HCl	1 40	0 00
4 *M* HCl	5 51	0 00
1 *M* H_2SO_4	1 68	0 00
4 *M* H_2SO_4	3 50	0 00
2 *M* $NaNO_3$	0 00	2 02
4 *M* $NaNO_3$	0 23	2 02
2 *M* KNO_3	0 09	1 55
0 05 *M* NaOH	4 58	3 50
0 1 *M* NaOH	Dissolved appreciably	Dissolved appreciably
0 1 *M* KOH	Dissolved appreciably	Dissolved appreciably
0 1 *M* NH_4OH	1 68	3 15
0 5 *M* NH_4OH	4 44	3 15

Ion-Exchange Capacity (i.e.c.)

The i.e.c. was determined as usual by the column process taking 1 g exchanger (H^+-form) in a glass tube of i.d. ~1 cm and maintaining the flow rate at ~0.5 mL/min. The total volume of the eluant necessary for the complete elution of H^+-ions was 250 mL and the values in meq/dry g for different metals were Li(I) 1.05, Na(I) 1.60, K(I) 1.49, Mg(II) 1.53, Sr(II) 1.59, Ca(II) 1.10, Ba(II) 1.61, NH_4(I) 0.8.

Thermal stability

Several 1.0-g portions of Sample S-6 were heated at various temperatures in a muffle furnace for 1 h each, and the i.e.c. was determined as above by the column process after cooling them to the room temperature. The i.e.c. was also determined after heating the sample for 4h at 400 and 800°C.

Elution Behavior

Since the extent of elution depends upon the concentration of the eluant, a fixed volume (125 mL) of $NaNO_3$ solution of varying concentrations was passed through a column containing 0.5 g of the exchanger. It was observed that a 1.0 *M* concentration is sufficient for the complete elution of H^+-ions from this column. The elution was therefore done with a 1.0 *M* solution of $NaNo_3$ as an eluant. Figure 1 shows the histograms of the γ-irradiated and unirradiated samples of Sb(V) silicate.

pH Titrations

These were performed by the Topp and Pepper's method (*19*) by placing 500 mg of the exchanger in several 250 mL conical flasks, followed by equimolar solutions of alkali metal chlorides in different volume ratios, the final volume being 50 mL. The pH was recorded after keeping the solutions overnight for equilibrium and was plotted against the milliequivalents of the OH^- added. The experiment was repeated for the irradiated sample and the results are summarized in Fig. 2.

Distribution Studies

For Some Common Metal Ions

250 mg of the exchanger in the H^+ form were shaken at 30 ± 2°C for 4 h with a 25-mL solution containing the metal ion. The initial and final concentrations of the metal ion in the solution were determined by EDTA titrations (*20*) as usual (*21*). The K_d values obtained are summarized in Table 3.

For Alkali Metals

The K_d values for Na(I), K(I), Rb(I), and Cs(I) were determined using radiotracers. For this purpose 100 mg of the material in the H^+ form equilibrated with 20-mL of the solvent containing 1.0 mL of the tracer and 1.0 mL of the carrier solution of the required concentration. The initial and final metal concentrations in solution were determined by measuring the activity of the solution in the two cases. The K_d values were calculated with the following formula:

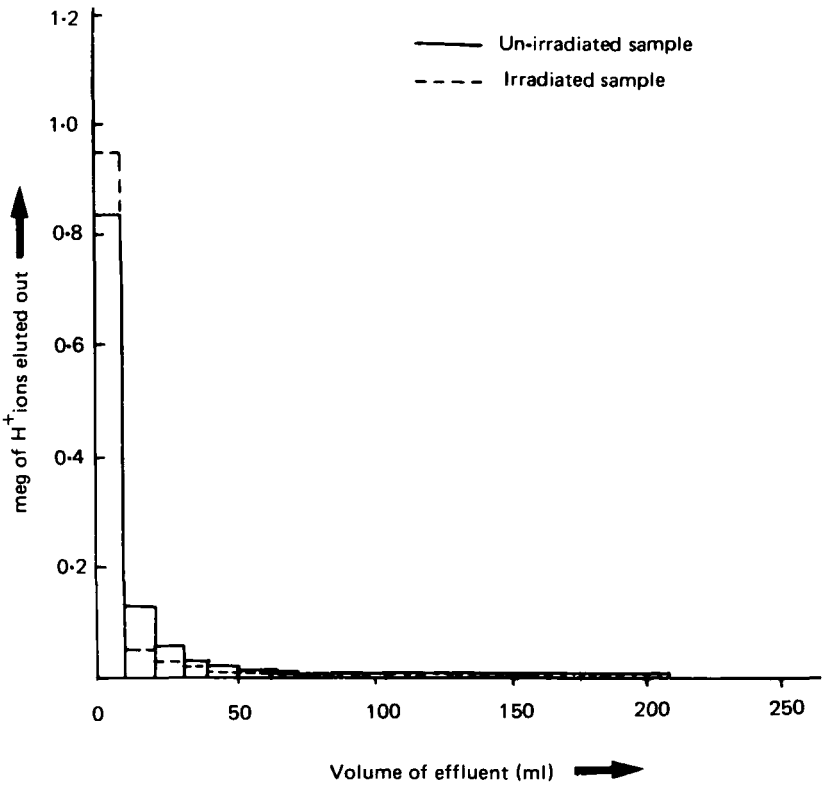

FIG. 1. Histograms showing the elution behavior of antimony(V) silicate exchanger.

$$K_d = \frac{I - F}{F} \times \frac{V}{M} \text{ mL/g}$$

where I = initial volume of the EDTA used or initial activity of the solution
F = final volume of the EDTA used or the final activity of the solution
V = volume of the solution
M = mass of the exchanger

The following radiotracers were used in these studies with their half-life periods shown in parentheses: ^{24}Na (15 h), ^{42}K (12.5 h), ^{86}Rb (18.7 d), ^{137}Cs (30.2 years), ^{54}Mn (31.3 d), and ^{203}Hg (46.6 d). Figure 3 shows the variation of K_d values with the pH for different alkali metals.

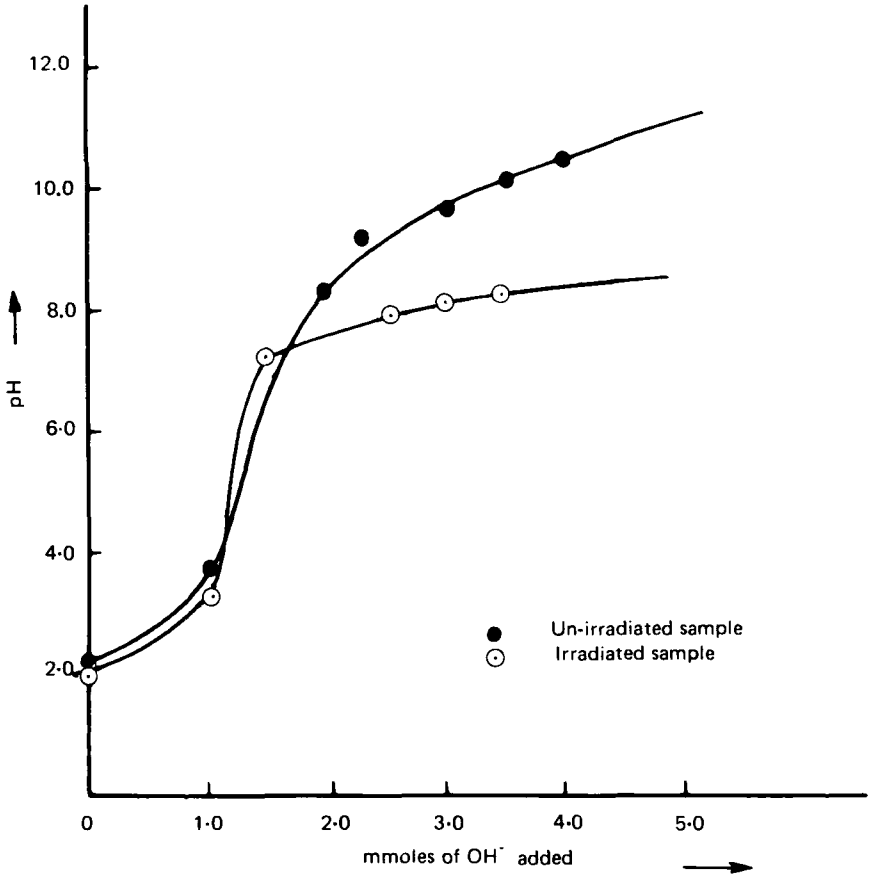

FIG. 2. pH titration curves for antimony(V) silicate.

Separations Achieved

Several binary separations were tried using a column containing 2 g of the sized (50-100 mesh) exchanger particles taken in a glass tube having an i.d. of ~0.6 cm. The flow rate was fixed as ~0.5 mL/min using eluants selected on the basis of the K_d values obtained.

RESULTS AND DISCUSSION

These studies reveal that antimony silicate is a highly stable and reproducible ion-exchange material. A comparison of its thermal stability

TABLE 3
K_d Values of Some Common Metal Ions on Antimony Silicate in Different Media[a]

Metal ion	Solvent pH	DMW 7	0.01 *M* $HClO_4$ 2	0.01 *M* $HClO_4$ 1	10% HCl + 25% DMSO (1:20) 1.6	10% HCl + 25% DMSO (1:10) 1.2	10% HCl + 25% DMSO (1:5) 0.9	10% HCl + 25% DMSO (1:1) 0.4
				K_d values				
Zn(II)		TA	1800	36	159	39	19	0
Cd(II)		TA	1900	1900	900	900	900	900
Hg(II)		TA	TA	1250	0	0	0	0
Mn(II)		TA	433	14	28	10	0	0
Mg(II)		TA	357	12	33	14	0	0
Ca(II)		TA	TA	TA	1500	1500	1500	357
Sr(II)		TA	TA	TA	TA	1350	1350	480
Ba(II)		TA	TA	1153	1153	616	526	150
Cu(II)		*TA*	*TA*	*255*	*220*	*52*	*18*	*0*
Ni(II)		TA	900	620	36	20	7	0
VO(II)		TA	866	16	45	32	16	0
Pb(II)		TA	TA	1400	TA	1400	1400	328
Co(II)		TA	655	54	78	54	36	13
Fe(III)		TA	TA	175	633	214	0	0
Al(III)		TA	TA	37	149	44	0	0
Zr(IV)		TA	TA	TA	800	1250	1250	1250
Th(IV)		TA	TA	600	1066	60	218	62
Y(III)		TA	TA	424	TA	424	1203	92
La(III)		TA	TA	572	TA	1000	450	312

[a]TA = total adsorption

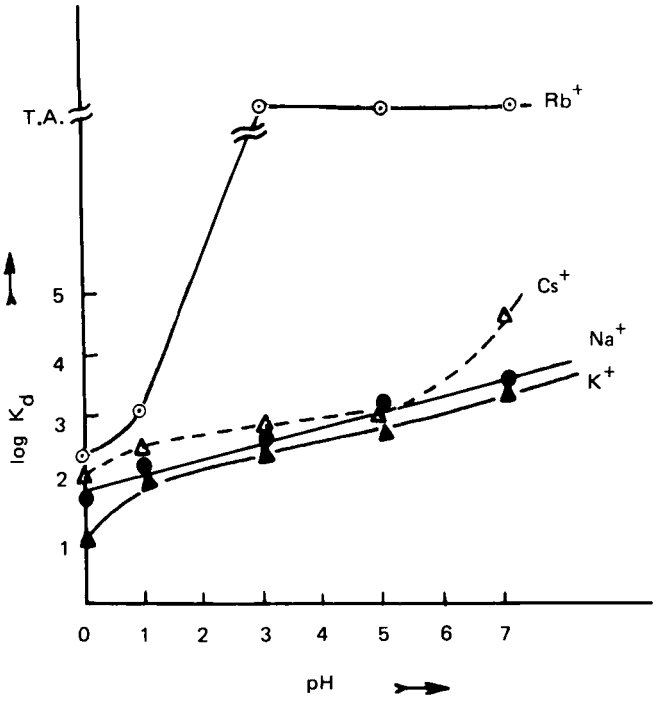

FIG 3 Effect of pH on the K_d values of alkali metals on antimony(V) silicate

with other exchangers of this class (Fig. 4) indicates a high percent retention in its i.e.c. on heating, almost comparable with the zirconium(IV) and titanium(IV) arsenophosphates prepared earlier (*21*). At 400°C, even heating for 4 h does not alter its i.e.c. appreciably, as seen in Table 4. This material also appears to be highly chemically stable (Table 2). The elution behavior indicates that the exchange is quite fast and almost all of the H^+-ions are eluted out in the first 50 mL of the effluent from a column of 1.0 g exchanger (Fig. 1). Moreover, the exchange takes place in one step as indicated by the pH titration curve shown in Fig. 2.

The distribution studies illustrate some of the interesting features of this material. A plot of pH versus log K_d for Na(I) and K(I) is a straight line; however, there is a positive deviation in this behavior for the Cs(I) ion above pH 5 (Fig. 3). For Rb(I), the material shows a total adsorption even above pH 1. In this respect, antimony silicate is different from Sn(IV) arsenophosphate (*22*) which shows a linear increase in K_d values for Rb(I) and Cs(I) with pH. Antimony silicate, therefore, appears to be specific for the Rb(I) ion and can be used for its extraction.

TABLE 4
Ion Exchange Capacity and Appearance of SbSi After Heating to Various Temperatures

Drying temperature (°C)	Time of heating (h)	Na ion exchange capacity (meq/dry g)	Appearance
45	1	1 60	White
100	1	1 52	White
300	1	1 42	Yellowish white
400	1	1 25	Yellowish white
600	1	1 20	Dark yellow
800	1	0 72	Yellowish white
400	4	1 18	Yellowish white
800	4	0 34	Yellowish white

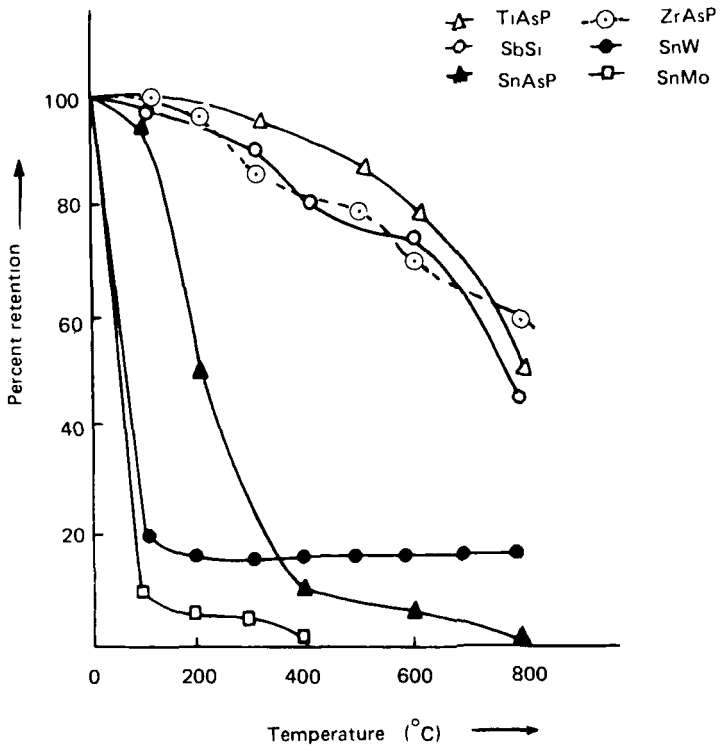

FIG 4 Percent retention of the H^+ ions in the exchanger phase on heating

On the basis of its chemical composition, pH titration, and TGA results, the antimony silicate, prepared in these studies, may be tentatively assigned the following formula: $[Sb_2O_5(H_2SiO_3)_6] \cdot nH_2O$

If it is assumed that all the exchangeable water molecules are removed on heating up to ~280°C, the first inflection point in the TGA curve (Fig. 5), the value of n can be calculated from

$$18n = \frac{X(M + 18n)}{100}$$

where X is the % weight loss (20%) in the exchanger on heating up to the inflection temperature and M is its molecular weight. The value of n thus obtained is 11. A further loss in weight above 280°C may be due to the

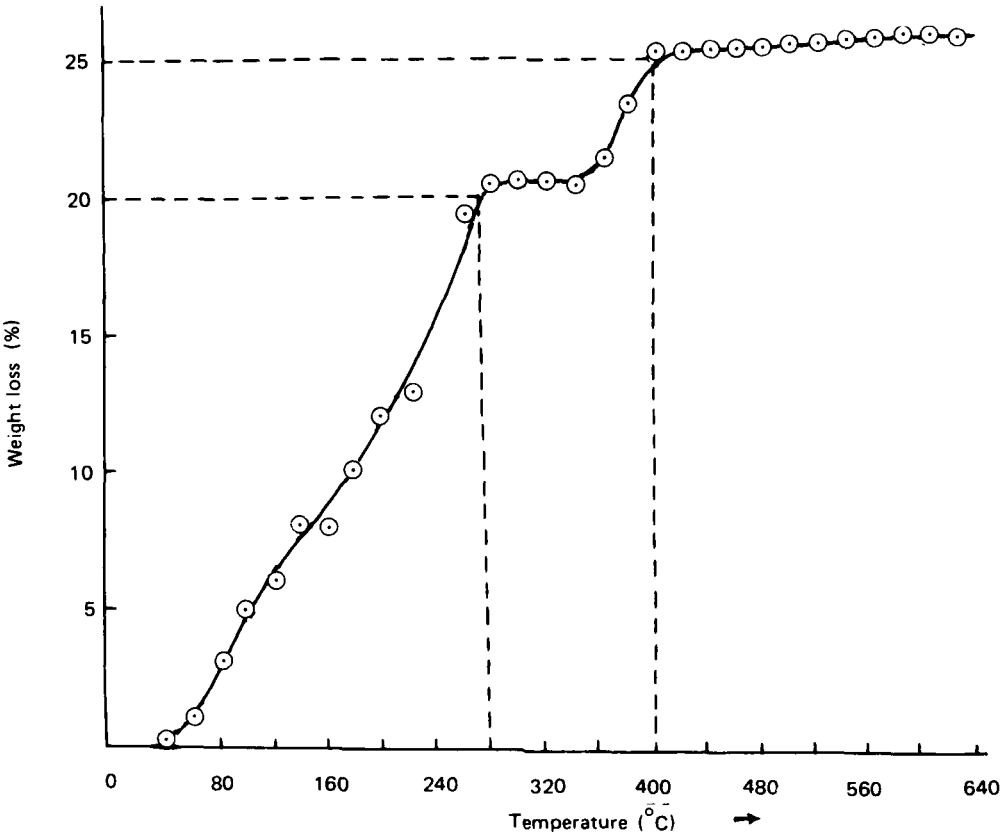

FIG. 5. Thermogram of antimony (V) silicate.

condensation process which probably continues up to 400°C, beyond which the oxides of Sb and Si are probably formed. An exhibition of the i.e.c. of SbSi even after heating to this temperature may be accounted for by the formation of antimonic acid when the oxide is dipped in aqueous solution. Antimonic acid has earlier been studied (*10, 23, 24*) as a cation exchanger.

The IR spectra show the peaks at ~450, 750, 1050, 1600, and 3300 cm^{-1} which represent (*25*) the presence of metal hydroxides (450 and 750) silicates (1050) and H_2O molecules (1600 and 3300) in the structure. The x-ray studies reveal the crystalline behavior of the material with a *d*-value 6.09 Å.

An irradiation of the sample by γ-rays for 96 h under a dose rate of 0.4 Mrd/h does not significantly change the ion-exchange behavior and the selectivity of metal ions as indicated in Table 5. Only a slight change in the elution rate (Fig. 1) and pH titration behavior (Fig. 2) is observed on irradiation.

The utility of this material was demonstrated by achieving separations of great analytical significance: for example, Mg(II) was separated from other alkaline earths (Figs. 6 and 7). Similarly, the rather difficult separation of Cd(II) from Zn(II) was performed on this ion-exchanger with a simple eluant 1 *M* $HClO_4$ (Fig. 8). Binary separations like Cd–Mn and Hg–Pb were achieved on the columns of SbSi. Although antimonic acid has earlier shown (*10*) a great affinity for Cd(II), it could not be utilized for its separation from Zn(II). For this purpose the SbSi exchanger prepared in these studies seems to have an added advantage. Table 6 shows the details of the six binary separations achieved on the column of this exchanger. It is clear from Table 6 that the % error observed in all cases is reasonably low and the separations can be said to be precise.

TABLE 5
Effect of Irradiation on the Adsorption of Mn^{2+}, Hg^{2+}, and Cs^{+} on SbSi

	K_d values			
	Water		$HClO_4$	
Metal ion	Normal sample	Irradiated sample	Normal sample	Irradiated sample
Mn^{2+}	473	515	34 0	44 0
Hg^{2+}	420	373	102	194
Cs^{+}	38,394	36,298	97	110

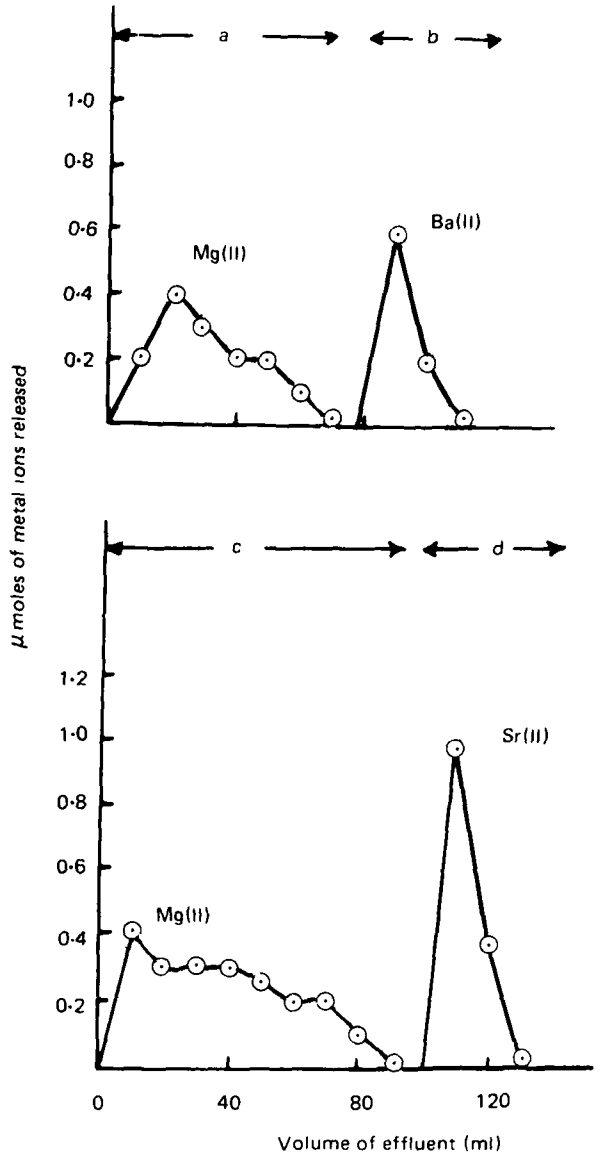

FIG 6 Separationof Mg(II) from Ba(II) and Sr(II) on antimony(V) silicate columns (a) and (c), 0 1 *M* $HClO_4$, (b) and (d) 1 *M* $HClO_4$

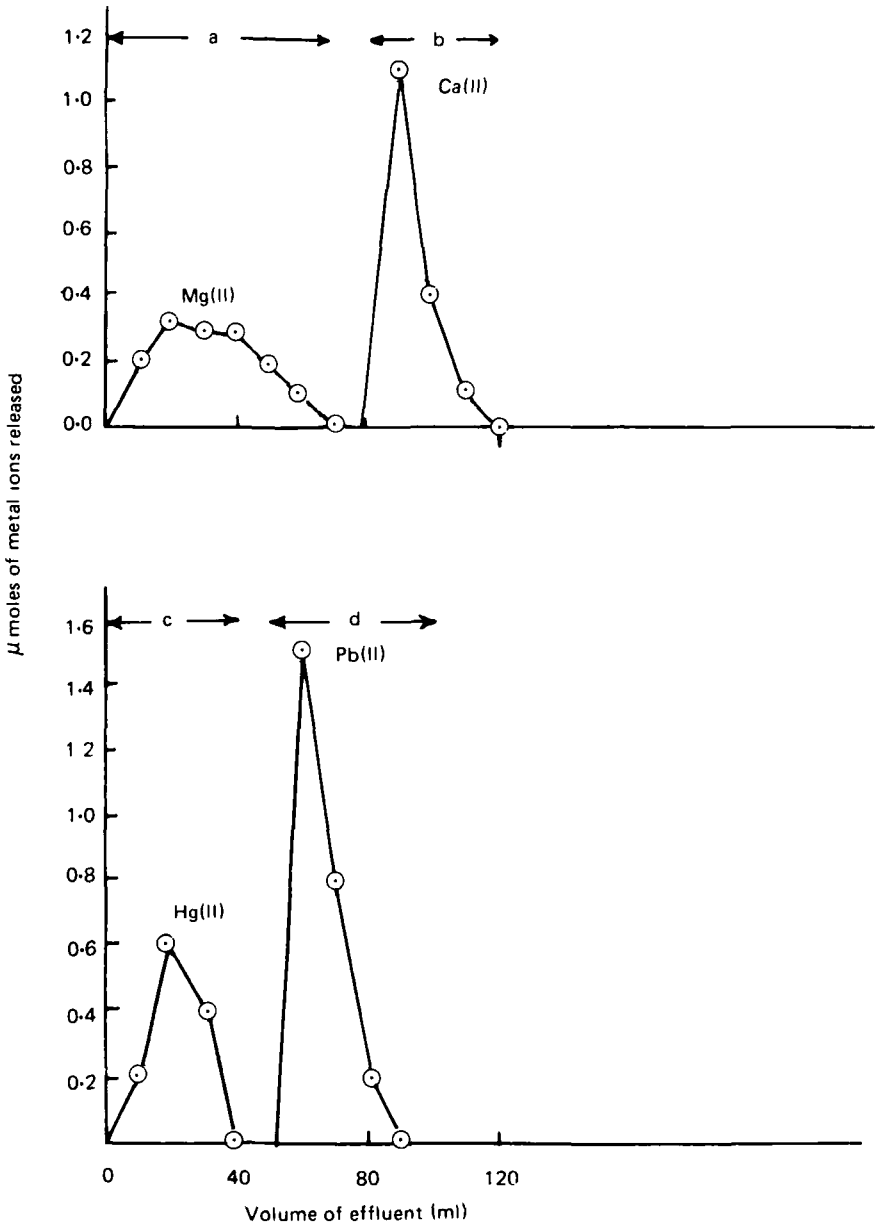

FIG 7 Separation of Mg(II) from Ca(II) and of Hg(II) from Pb(II) on antimony(V) silicate columns (a), 0 1 *M* $HClO_4$, (b) and (d), 1 *M* $HClO_4$, (c) 10% HCl + 5% DMSO

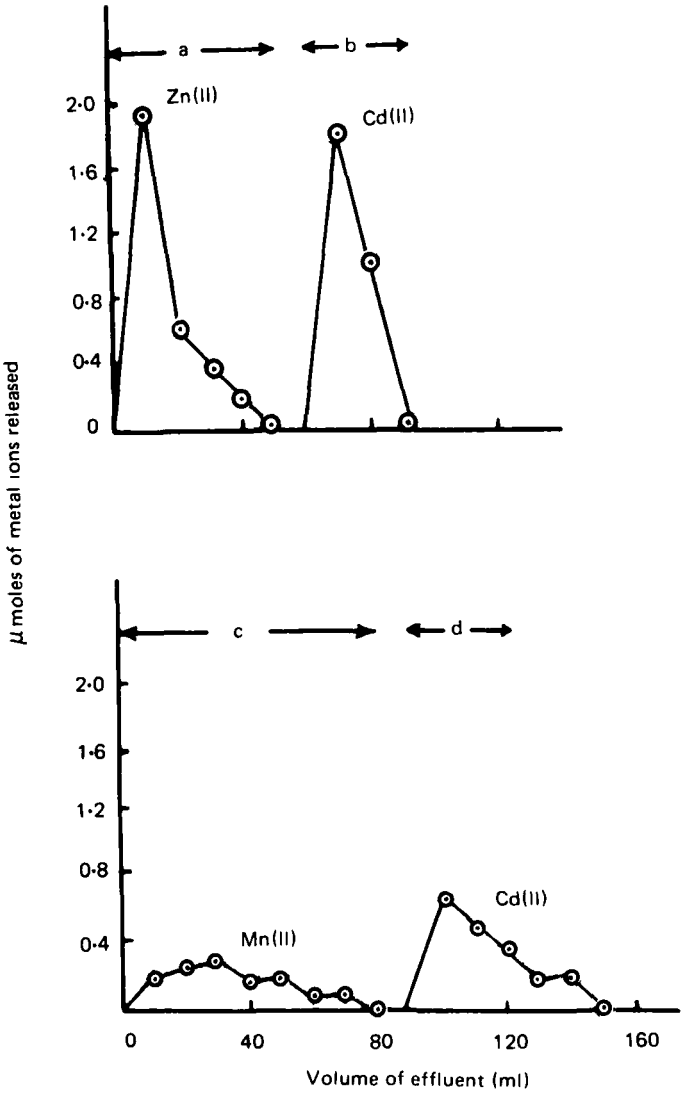

FIG. 8. Separation of Cd(II) from Zn(II) and of Mn(II) on antimony(V) silicate columns: (a) and (c), 0.1 *M* $HClO_4$; (b) and (d), 1 *M* $HClO_4$.

TABLE 6
Binary Separations Achieved on Antimony(V) Silicate Columns

Sample	Separations achieved (M_1 M_2)	Amount taken (μg)		Amount found (μg)		Error (%)		Eluent and its volume used for different metals
		M_1 (μg)	M_2 (μg)	M_1 (μg)	M_2 (μg)	M_1	M_2	
1	Zn–Cd	200 0	304 0	204 0	309 0	0 0	+1 6	Zn 0 1 *M* $HClO_4$, 50 mL Cd 1 *M* $HClO_4$, 30 mL
2	Mn–Cd	71 0	187 0	67 0	187 0	−5 6	0 0	Mn 0 1 *M* $HClO_4$ 80 mL Cd 1 *M* $HClO_4$ 60 mL
3	Hg Pb	240 0	517 0	240 0	497 0	0 0	−3 8	Hg 10% HCl + 5% DMSO, 40 mL Pb 1 *M* $HClO_4$, 40 mL
4	Mg Ca	34 0	64 0	35 0	64 0	+2 6	0 0	Mg 0 1 *M* $HClO_4$, 70 mL Ca 1 *M* $HClO_4$ 50 mL
5	Mg–Ba	34 0	112 0	34 0	112 0	0 0	0 0	Mg 0 1 *M* $HClO_4$, 50 mL Ba 1 *M* $HClO_4$ 60 mL
6	Mg Sr	48 0	123 0	49 0	123 0	+2 0	0 0	Mg 0 1 *M* $HClO_4$, 80 mL Sr 1 *M* $HClO_4$ 20 mL

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Kinetics of Exchange of Alkaline Earth Metals on Antimony(V) Silicate Cation Exchanger

K G VARSHNEY* & SIMA RANI
Chemistry Section, Faculty of Engineering & Technology, Aligarh Muslim University, Aligarh 202001

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A kinetic study has been performed applying the Nernst-Planck equation to the Mg^{2+} H^+, Ca^{2+} H^+, Sr^{2+} H^+ and Ba^{2+} H^+ exchange reactions on antimony(V) silicate cation exchanger at four different temperatures, viz. 25, 33, 50 and 65°C under the conditions favouring a particle diffusion controlled phenomenon only. The rate of exchange has been found to be independent of the metal ion concentration at and above the value $2 \times 10^{-2} N$. The self diffusion coefficients (D_0), activation energies (E_a) and entropies of activation (ΔS^*) have also been calculated, which are useful for predicting the ion-exchange phenomenon taking place in the material.

Antimony(V) silicate has been synthesized in our laboratories[1] as a crystalline material possessing appreciable cation-exchange capacity. Since the kinetic studies of a reaction help in understanding its mechanism, it is worthwhile to conduct such studies on the exchange process taking place on antimony(V) silicate, in view of its peculiar behaviour. The studies[2-9] made so far in this direction are based on the old B_t criterion which is of limited use because of the different mobilities[10] of the exchanging ions involved. In such cases Nernst-Planck equations[11,12] should be used to obtain more precise values of the various kinetic parameters. We report here the results of such a study.

Materials and Methods

Antimony pentachloride used in this study was a Kochlight product and sodium silicate was a Riedel product. Other reagents and chemicals were BDH reagents of AR grade.

A water-bath incubator shaker having a temperature variation of ±0.5°C was used for the equilibrium studies.

Synthesis of antimony(V) silicate

It was synthesized by the method reported earlier[1].

Kinetic measurements

The rates of exchange were measured by the limited bath technique[13] on the exchanger particles of mean radii ~250 μm (50-70 mesh size). 20 ml fractions of the metal ion solution of constant ionic strength ($2 \times 10^{-2} N$) were shaken with the exchanger (0.2 g) in a temperature controlled shaker at various temperatures (25, 33, 50 and 65°C) for different time intervals. The supernatant liquid was removed immediately by filtration through Whatman No.4 filter paper and the metal ions were determined in the solution with EDTA titration[14] using Eriochrome Black-T as an indicator.

Results and Discussion

A study of the concentration effect on the rate of exchanger for Mg^{2+}-H^+ exchange at 33 C shows that at a concentration $< 2 \times 10^{-2} N$, the initial rate of exchange is proportional to $[Mg^{2+}]$. At a concentration $\geq 2 \times 10^{-2} N$, it is found to be independent of the metal ion concentration. Under the conditions of particle diffusion control, a relatively large particle size of the exchanger and vigorous shaking, the fractional attainment of equilibrium is given by Eq. 1,

$$U(\tau) = \frac{\text{the amount of exchange at time } t}{\text{the amount of exchange at infinite time}} \quad \ldots (1)$$

A plot of $U(\tau)$ versus t (Fig. 1) indicates that the fractional attainment of equilibrium is faster at higher temperatures, an observation analogous to that obtained for the other materials of this class[3-8]. Although this is a limited bath system, the equation applicable to an infinite bath can be used here because $CV \gg \bar{C}\bar{V}$ where C and $\bar{C}$ are the metal ion concentrations in the solution and exchanger phases respectively, while V and $\bar{V}$ are the volumes of these phases. The Nernst-Planck equations can be solved with some additional assumptions[15], which are valid for inorganic ion-exchangers as the swelling changes and the specific interactions are not significant in this case. As a result we obtain a coupled inter-diffusion coefficient $\bar{D}_{AB}$, the value of which depends on the relative concentrations of the counter ions A and B in the exchanger phase ($\bar{C}_A$ and $\bar{C}_B$). For $\bar{C}_A \ll \bar{C}_B$ the inter-diffusion coefficient assumes the value $\bar{D}_A$, A being the counter ion initially present in the ion-exchanger phase. Since in the present study the

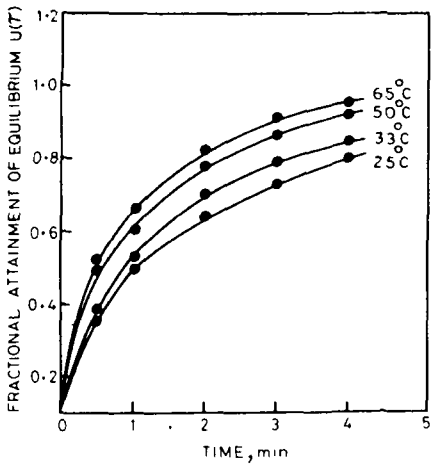

Fig. 1—Plots of $U(\tau)$ against time for Mg(II) at different temperatures on antimony(V) silicate

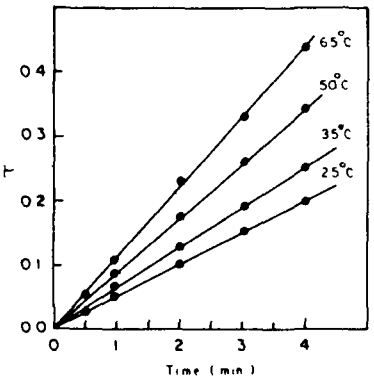

Fig. 2—Plots of τ versus time for Mg^{2+} ion at different temperatures on antimony(V) silicate

exchanger is taken in the H^+ form, $\bar{D}_A$ may be replaced by $\bar{D}_H$.

Thus, on the basis of the Nernst-Planck equations the numerical results can be expressed by the explicit approximation[16],

$$U(\tau)=\{1-\exp[\pi^2(f_1(\alpha)\tau+f_2(\alpha)\tau^2+f_3(\alpha)\tau^3)]\}^{1/2} \quad \ldots (2)$$

where $\tau=(\bar{D}_H t)/r_0^2$, the mobility ratio $\alpha=\bar{D}_H/\bar{D}_M$, r_0 = particle radius, and D_M is the inter-diffusion coefficient of the metal ion. The α values for the different metal ions studied are α_{Mg} = 6.5818, α_{Ca} = 5.8387, α_{Sr} = 5.8387 and α_{Ba} = 5.4848. Under the conditions $1 \leqslant \alpha \leqslant 20$ and Z_H/Z_M = 0.5, which are fulfilled in the present case, the three functions $f_1(\alpha)$, $f_2(\alpha)$ and $f_3(\alpha)$ can be expressed as:

$$f_1(\alpha)=-\frac{1}{0.64+0.36\alpha^{0.668}} \quad \ldots (a)$$

$$f_2(\alpha)=-\frac{1}{0.96-2.0\alpha^{0.4635}} \quad \ldots (b)$$

$$f_3(\alpha)=-\frac{1}{0.27+0.09\alpha^{1.14}} \quad \ldots (c)$$

Table 1—Slopes of the Various τ Versus Time Plots for Alkaline Earths

Metal ion	$s \times 10^4 (s^{-1})$ at temp.			
	25 C	33 C	50 C	65 C
Mg^{2+}	8.33	10.42	14 17	18.33
Ca^{2+}	3.61	4 17	5.00	6.25
Sr^{2+}	3.33	5 00	5 40	6 83
Ba^{2+}	5.21	6.25	8.17	9 44

Each value of $U(\tau)$ will have a corresponding value of τ which can be obtained on solving Eq. 2 by the graphical method. The plots of τ versus t at four different temperatures (Fig. 2) for the Mg^{2+} ion are shown at a concentration $2.0 \times 10^{-2} N$. The plots are linear passing through the origin thus confirming the presence of a particle diffusion controlled phenomenon. The slopes (s) of such lines for all the four alkaline earth metal ions are given in Table 1. The slopes are related with $\bar{D}_H$ (Eq. 3),

$$s=\frac{\bar{D}_H}{r_0^2} \quad \ldots (3)$$

The values of $\bar{D}_H$ obtained from Eq. (3) were plotted against 1/T (Fig. 3) when straight lines were obtained verifying the Arrhenius relation (Eq. 4),

$$\bar{D}_H=D_0\exp(-E_a/RT) \quad \ldots (4)$$

D_0 was obtained by extrapolating these curves and observing the intercept at the origin. The activation energy (E_a) was then calculated with the help of Eq. (4) taking the value of $\bar{D}_H$ as 273°K. The entropy of activation was then calculated by using Eq. 5.

$$D_0=2.72\,d^2\,kT/h\exp\left(\frac{\Delta S^*}{R}\right) \quad \ldots (5)$$

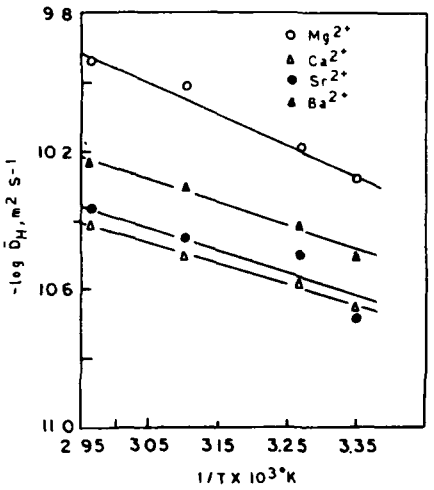

Fig. 3—Plots of $\log \bar{D}_H$ versus 1/T for alkaline earth metal ions on antimony(V) silicate

Table 2—Self-diffusion Coefficients, Energies of Activation and Entropies of Activation of Alkaline Earth Metals on Antimony(V) Silicate

Migrating ion	Hydrated ionic radii (Å)	D_0 (m^2s^{-1})	E_a ($kJ\,mol^{-1}$)	ΔS^* ($JK^{-1}mol^{-1}$)
Mg^{2+}	3.10	6.03×10^{-9}	12.18	−53.74
Ca^{2+}	2.00	6.03×10^{-10}	8.42	−72.88
Sr^{2+}	1.80	8.32×10^{-10}	9.04	−70.21
Ba^{2+}	1.50	1.10×10^{-9}	9.05	−67.88

is similar to that observed earlier for tantalum arsenate[3] and ferric antimonate[5].

Here d is the ionic jump distance (taken[17] as 5Å), k is the Boltzmann constant and h is the Planck's constant. T was taken as 273°K. The values of D_0, E_a and ΔS^* are summarized in Table 2. The results indicate that the E_a and ΔS^* values are related, to some extent, with the hydrated ionic radii of the alkaline earths. Negative ΔS^* values confirm that the behaviour of Sb(V) silicate

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